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AN

ELEMENTARY

MANUAL OF CHEMISTRY.

ABRIDGED FROM

ELIOT AND STORER'S MANUAL,

WITH THE CO-OPERATION OF THE AUTHORS.

BY

WM. RIPLEY NICHOLS,
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REVISED EDITION.

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EXTRACT FROM THE PREFACE TO ELIOT AND STORER'S MANUAL OF INORGANIC CHEMISTRY.

"In preparing this manual, it has been the authors' object to facilitate the teaching of chemistry by the experimental and inductive method. . . . The authors believe that the study of a science of observation ought to develop and discipline the observing faculties, and that such a study fails of its true end if it become a mere exercise of the memory.

"The minute instructions, given in the descriptions of experiments and printed in the smaller type, are intended to enable the student to see, smell and touch for himself; these detailed descriptions are meant for laboratory use. In order to mark as clearly as possible the distinction between chemistry and chemical manipulation, the necessary instructions on the latter subject have been put in an Appendix. In cases in which it is impossible for every student to experiment for himself, the authors hope that this manual will make it easy for the teacher, even if he be not a professional chemist, to exhibit to his class, in a familiar and inexpensive manner, experiments enough to supply ocular demonstration of the leading facts and generalizations of the science. . . .

"There is little original in the book except its arrangement and method, in part, and its general tone. The authors have, of course, drawn largely from the invaluable compilations made by Gmelin, Otto and Watts, and they have also availed themselves freely of the text-books of Stoeckhardt and Miller, and the writings of Hofmann."

PREFACE TO THE ABRIDGMENT.

THIS Abridgment, which is not simply an abridgment, is a shorter and easier, yet a more comprehensive manual than the original one. The larger manual covers only inorganic chemistry; the Abridgment includes the elements of what is generally called organic chemistry. The chapter on Carbon in the original manual has been subdivided and expanded, so as to comprehend the principal facts and theories of that part of chemistry which in most text-books is treated as a distinct branch under the name of organic chemistry. In this way the compounds of carbon are studied in their natural place and order, and the student has a fairer view of the whole science than he is likely to get when the great majority of the carbon compounds are studied quite apart from carbon itself and from some of its longest-known compounds, and after all the other elements.

In preparing the new chapters on the compounds of carbon, the authors have made free use of the works mentioned above, especially of the text-books of Stoeckhardt and Miller; they would also acknowledge indebtedness to Prof. Johnson's "How Crops Grow," from which several of the experiments have been taken. These experiments, as well as the others in these chapters, are such as have been found to stand the test of actual performance by students.

This manual is written in the interest of no particular theory; the typical formulæ have been employed in many cases in the chapters on carbon, as affording a convenient method of representing the reactions in which the compounds take part. Teachers who desire to illustrate more fully the theory of the subject may refer to Cooke's Chemical Philosophy, from which some useful hints have been taken in preparing this Abridgment.

Teachers who put the Abridgment into the hands of their pupils will find it useful to consult the larger manual for additional facts and experiments and fuller explanations.

MARCH, 1872.

PREFACE TO THE SECOND REVISED EDITION.

FROM time to time since the first issue of the book, corrections have been made of such errors as have come to the notice of the authors. The present edition has been thoroughly revised. The most important changes in the first revised edition were in Chapters IX and XI, and in §§ 27, 28, 36, 63, and 76; some new matter was also added. In the present edition, besides minor corrections and additions, Chapter VI has been rewritten. The page numbers, however, as a rule, have not been altered, so that where the book is already in use there will be no difficulty in the way of the gradual introduction of this new edition.

JUNE, 1880.

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ELEMENTARY

MANUAL OF CHEMISTRY.

INTRODUCTION.

1. THE various objects which constitute external nature present to the observing eye an infinite variety of quality and circumstance. Some bodies are hard, others soft; some are brittle, others tough or elastic. Some natural objects are endowed with life, — they grow; others are lifeless, — they may be moved, but do not move themselves. Some bodies are in a state of incessant change; while others are so immovable and unchangeable that they seem everlasting. In the midst of this infinite diversity of external objects, where lies the domain of **Chemistry**? What is the subject-matter of this science?

When air moves in wind, when water moves in tides or in the fall of rain or snow, the air and water remain air and water still; their constitution is not changed by the motion, however frequent or however great. A bit of granite, thrown off from the ledge by frost, is still a bit of granite, and no new or altered thing. If a solid piece of iron be reduced to filings, each finest morsel is metallic iron still, of the same substance as the original piece, as will appear to the eye, if a morsel be sufficiently magnified under the microscope. The melted, fluid lead in the hot crucible, and the solid lead of the cold bullet cast from it, are the same in substance, only differing in respect

to temperature. In all these cases, the changes are external and non-essential, not intimate and constitutional: they are called **physical** changes.

2. When iron is exposed to the weather, it becomes covered with a brownish, earthy coating, which bears no outward resemblance to the original iron; and, if exposed long enough, the metal completely disappears, being wholly changed into this very different substance, *rust*. A piece of coal burns in the grate and soon vanishes, leaving nothing but a little ashes. Dead vegetable or animal matters, buried in the ground, soon putrefy, decay, and disappear. So, too, the fragment of granite which frost has broken from the ledge, exposed for centuries to the action of air and rain, becomes changed; it "weathers," and after a time could no longer be recognized as granite. All these changes involve alterations in the intimate constitution of the bodies which undergo them: they are called **chemical** changes.

Experiment 1. — Mix thoroughly 3 grammes (for Tables of the Metrical System of Weights and Measures, see Appendix) of coarsely-powdered sulphur with 8 grammes of copper-filings or fine turnings.

Fig. 1.

Put the mixture into a tube of hard glass, No. 3, about 12 centimetres long, and closed at one end. (For the manipulation of tubing, see Appendix, §§ 1–4.) Hold the tube by the open end with the wooden nippers, as in Fig. 1, and heat the mixture over the gas-lamp (Appendix, § 5), until it suddenly glows vividly at the instant when the copper and sulphur combine.

Before heat was applied, the mixture of the two substances was simply mechanical, and the copper might have been completely separated from the sulphur, by due care and patience; but, during the ignition, the copper and sulphur have united chemically, and there has been formed a substance, which, while containing both, has no external resemblance to either. In the new body the eye can detect neither copper nor sulphur.

Processes by which the whole character and appearance of

the bodies concerned are changed, as in this experiment, so that essentially new bodies are formed from the old, are **chemical processes.** It is the function of the chemist, on the one hand, to investigate the action of each substance on every other, and to study the properties of the combinations resulting from this action; and, on the other, to separate compound bodies into their simpler constituents: he further seeks the general laws by which the intimate combinations of matter are controlled. With these ends in view, he endeavors to pull to pieces, or, in technical language, to **analyze,** every natural substance on which he lays hands. Having thus found out the composition of the substance, he seeks to put it together again, or to recompose it out of its constituent parts. By one or both of these two processes, — **analysis** (unloosing) and **synthesis** (putting together), — the chemist studies all substances.

3. The first question which the chemist asks himself concerning every natural substance is, *Of what is it composed?* He then attempts to resolve the substance into simpler constituents. If he succeeds in decomposing it, he obtains the answer to this first question; if the body can not be decomposed by any known method of analysis, the substance must be regarded as being already at its simplest. Such simple bodies are called **elements.** Secondly, the chemist asks, *How does this new substance comport itself when brought into contact with other substances already familiar?* Between sixty and seventy substances are at present admitted to be simple, primary substances, or elements; other elementary substances may hereafter be discovered, and substances which are now regarded as elements may hereafter be found to be compound; so that the number of the substances considered as elements is subject to change. Of compound bodies, formed by the union of these elements with each other, we find a series, numbering many thousands, in the inorganic kingdom of nature, comprising all the diversified mineral constituents of the earth's crust; while another series, far more complex in composition, and almost innumerable in multitude, exists in the vegetable and animal world. The task of the chemist in thoroughly answering his second question

would clearly be endless, were it not for the existence of general properties common to extensive groups of both elementary and compound bodies, and of general laws which chemical processes invariably obey.

While, therefore, the chemist seeks the answers to the two fundamental questions above stated, he is at the same time inquiring what relations exist between the properties of a body and its composition; and he is also studying that natural and invariable sequence of chemical phenomena, which, when fully known, will constitute the perfect science of chemistry.

4. Generalizations from observed facts, so long as they are uncertain and incomplete, are called **hypotheses** and **theories**; when tolerably complete and reasonably certain, they are called **laws**. The attention of the student should be constantly directed to the keen discrimination between *facts* and the *speculations* founded upon those facts; between the actual evidence of our trained senses brought intelligently to bear upon chemical phenomena, and the reasonings and abstract conclusions based upon this evidence; between, in short, that which we may know and that which we may believe.

CHAPTER I.

AIR.

5. We are everywhere surrounded by an atmosphere of invisible gas, called **air**. In motion, it is wind, and we recognize its existence by its powerful effects; but in the stillest places it exists as well. The presence of air in any bottle, flask or other hollow vessel which is empty, in the sense in which this word is ordinarily applied, can be shown very simply by attempting to put some other substance into the vessel, under such conditions that the air can not pass out from it.

If, for example, we wrap around the throat of a funnel with narrow outlet, a strip of moistened cloth or paper, so that the funnel shall fit

tightly into the neck of a bottle, and then fill the funnel with water, we shall observe that this water does not run into the bottle. The bottle which we have called empty is in reality filled with air, and it is this air which prevents the water from entering the bottle. If, now, the funnel be lifted slightly, so that the mouth of the bottle shall no longer be completely closed by it, the air within the bottle will pass out, and the water in the funnel will instantly flow down.

6. We may actually pump the air out of the bottle by means of an apparatus known as the air-pump ; or we may remove a portion of the air by suction.

Exp. 2. — Fit to any small flask or bottle a perforated cork (for the manipulation of corks, see Appendix, § 9), to which has been adapted a short piece of glass tubing, No. 7. Slip over the end of this glass tube a short piece of caoutchouc tubing. Suck part of the air out of the flask, and then nip the caoutchouc tube with thumb and finger, so that no air shall re-enter. Immerse the neck of the flask in a basin of water, and release the caoutchouc tube. Water will instantly rise into the flask to take the place of the air which has been sucked out.

7. The water, in this experiment, is forced into the flask by the pressure of the superincumbent atmosphere. Air has weight, a litre of dry air, at the temperature of 0°, weighing 1.2932 gramme. It has been determined that the force with which the air is attracted to the earth is on an average equal to a weight of 1.033 kilogramme to the square centimetre of surface. That is to say, the ocean of air above us presses down upon every square centimetre of the earth's surface with a force equal to that which would be exerted by a bar of metal, or other substance, a centimetre square in section and long enough to weigh 1.033 kilogramme. If such a bar were constructed of iron, it would be 1.3 metre long ; if of water, — and a bar of this substance can readily be made by enclosing the water in a tube, — it would be 10.33 metres long.

In addition to the qualities already mentioned, we find air to be tasteless and odorless ; it is also colorless when in small depths, but exhibits a blue tint when seen in large masses, as when in the absence of clouds we look at the sky or at a distant mountain.

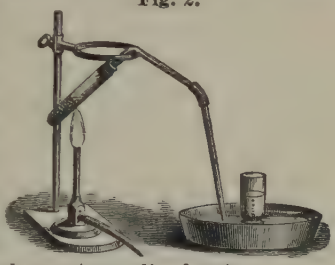
8. We will now proceed to study the **chemical properties** of air, first asking the question, *Of what is air composed?* When a bar of iron is heated in the air, as at a blacksmith's forge, it becomes covered with a coating, which flies off in scales when the iron is beaten upon the anvil. If a piece of wire or ribbon made of the metal *magnesium* be touched with a match, it will take fire and burn, and be entirely converted into white ashes. With the exception of gold, silver, platinum and a few other exceedingly rare metals, all the metals burn, or rust, when heated in the air. If no air be present, this rust or ashes will not be formed, however long or intensely the metal may be heated. But in what manner is the rust formed? Is something driven out of the metal into the air, or does something come out of the air and unite with the metal? This question may be answered by experiment. If a weighed quantity of tin-foil be heated in a porcelain dish over the gas-lamp, the metal is gradually converted into white ashes. When all the metal has thus been changed, and the ashes have been allowed to cool, it will be found that the ashes are very sensibly heavier than the original metal.

9. It is possible that during the heating the metal may have lost something, but it is certain that it has gained more. We have, therefore, taken something out of the air, which, gaseous in the air, has become solid in the white ashes of the tin. It would be possible to recover from the tin-rust the something thus taken from the atmosphere, and to compare it with common air, and so learn whether the matter which combined with the heated tin is air itself, or only a part of the air. The process, however, would be a circuitous one. From the rust of other common metals, as from that of mercury, for example, the absorbed gas can be very easily expelled. If metallic mercury be heated for a long time in the air, it will be entirely converted into a red substance known as "**red oxide of mercury.**"

Exp. 3. — Put into a tube of hard glass, No. 2, about 12 c. m. long, 10 grammes of the red mercury oxide. Tubes of hard glass, for such

purposes, will be hereafter designated as "ignition-tubes." Attach to this ignition-tube, by means of a perforated cork or caoutchouc stopper, a delivery-tube of glass, No. 8, of such shape and length that it shall reach beneath the inverted saucer in the pan of water, as represented in Fig. 2; the lower end of the ignition-tube should be about 4 c. m. above the top of the lamp. The tube may be supported on the iron stand, and should be inclined as represented in the figure. (For a description of the pneumatic trough, see Appendix, § 11.)

Fig. 2.



Upon heating the ignition-tube, gas will begin to escape from the delivery-tube, and bubble up through the water. The first portion is simply the atmospheric air which filled the tubes at the beginning of the experiment, and which is expanded by heat. This air may be collected in a small bottle by itself, and thrown away. The volume of gas thus thrown away should not be much greater than that of the tubes. As the ignition-tube becomes hotter, gas will be freely given off from the mercury oxide contained in it, and should be collected in bottles of 100 to 150 c. c. capacity.

It is necessary to avoid heating intensely any single small spot of the ignition-tube, lest the glass soften, and, yielding to the pressure from within, blow outward, and so spoil the tube and arrest the experiment. The gas-flame should be so placed and regulated as to heat 3 or 4 c. m. of the tube at once.

As soon as the disengagement of gas slackens, lift the iron stand up, and take the delivery-tube out of the water, taking care that no water remains in the end of the tube. Then, *and not till then*, extinguish the lamp. (See Appendix, § 11.) In the upper part of the ignition-tube, and sometimes in the delivery-tube also, metallic mercury will be found condensed in minute globules. The liquid metal is volatile at the temperature to which it has been subjected, and has distilled away from the hot part of the tube, and condensed upon the cooler part.

If a lighted splinter of soft wood be introduced into a bottle of the gas just collected, it will burn with much greater brilliancy than in the air. If a candle which has just been extinguished be thrust, while the wick still glows, into another bottle of the gas, the glowing wick will burst into flame, and the candle will burn with extraordinary brightness.

10. It is very obvious, from these experiments, that the gas which enters into the composition of mercury-rust is not air itself; but, since it came originally from the air, if it is not the whole of air, it must be a part of air. It has, indeed, been found to be a constant constituent of the air, and a **chemical element** of very various powers and great importance. It is called **oxygen**, and under this name will form the subject of the next chapter.

11. If oxygen be not air itself, but only a constituent of air, it follows that air must have other constituents, or, at least, one other constituent. If mercury be heated for a long time in contact with a certain confined portion of air, it will abstract from this air all of the oxygen, and there will be left a gas differing from both oxygen and common air. It is unfit for the support of combustion and of animal life; a candle is instantly extinguished by it, as if plunged in water; and small animals, thrust into the gas, die in a few seconds. The gas is, in reality, a second elementary substance, distinguished by marked chemical and physical peculiarities. It is called **nitrogen**, and under this name will be more completely studied in another chapter.

If the experiment be so conducted that the bulk of the original air, and also that of the residual nitrogen, can be measured, it will be found that the latter gas occupies four-fifths as much space as the air did at the beginning of the experiment. Besides oxygen and nitrogen, minute quantities of two or three other gases are found in the air, either uniformly or occasionally; but the amount of these gases is relatively very small, and they will not be considered at present.

The air, then, is not an element, but is a **complex** substance; and its two principal ingredients are the elementary bodies, **oxygen** and **nitrogen**, mixed in the proportion of four measures of nitrogen to one of oxygen.

CHAPTER II.

OXYGEN.

12. **Oxygen** gas may be obtained, as has already been seen, by heating mercury oxide : it may, however, be prepared in a variety of ways ; among others, and very conveniently, by heating a mixture of potassium chlorate and manganese binoxide, — two chemical substances whose constitution will be studied hereafter.

Exp. 4. — Mix intimately 5 grammes of potassium chlorate with 5 grammes of "black oxide of manganese," which has been previously well dried. Place the mixture in a tube of hard glass, No. 1, 12 or 15 c. m. in length. Attach to this ignition-tube, by means of a perforated cork or caoutchouc stopper, a delivery-tube of glass, No. 7, as represented in Fig. 2, and described upon page 7. Heat the mixture in the ignition-tube, and collect the gas which will be given off in bottles or jars of the capacity of about 250 c. c. The first 100 c. c. or so of gas should be rejected, since it will be contaminated with the air originally contained in the apparatus.

In performing this experiment, the following precautions should be observed. 1. Both the potassium chlorate and the manganese binoxide should be perfectly dry and pure ; that is, free from moisture, dust or particles of organic matter. 2. As soon as the oxygen begins to be delivered, the heat beneath the ignition-tube should be diminished, if need be, and so regulated that the evolution of gas shall be tranquil and uniform. 3. The uppermost portions of the mixture should be heated before the lower. 4. The ignition-tube should never be filled to more than one-third its total capacity, lest particles of solid matter be projected into the delivery-tube, and the outlet for the gas be thus stopped. 5. The ignition-tube should always be inclined as represented in Fig. 2, and never placed upright in the flame.

13. **Oxygen** is a transparent and colorless gas, not to be distinguished by its aspect from atmospheric air. Like air, it has neither taste nor smell. It is, however, somewhat heavier than air. If the weight of a measure of air be taken as 1,

then the weight of the same measure of oxygen is found to be 1.1056. One of its most striking characteristics is its power of making things burn. This has been already illustrated in **Exp. 3, § 9.**

If a piece of phosphorus the size of a small pea, having been well dried between pieces of blotting-paper, is placed in a deflagrating-spoon, touched with a hot wire or a lighted match, and then thrust into a jar of oxygen, it will burn with intense brilliancy, and with the formation of a dense white smoke. The following experiments will still further illustrate this property of oxygen : —

Fig. 3.

Exp. 5. — Place in a deflagrating-spoon (see Appendix, § 13) a bit of sulphur as large as a pea. Light the sulphur, and thrust it into a bottle of oxygen. It will burn with a beautiful blue flame, and much more brilliantly than in air. A suffocating gas is at the same time produced.

Exp. 6. — Place a piece of charcoal — that of bark is best — in a deflagrating-spoon. Kindle the charcoal by holding it in the flame of a lamp, and then introduce it into a bottle of oxygen. It will burn vividly, throwing off brilliant sparks if bark-charcoal had been employed. In this experiment, as in the preceding, the products of the combustion are obviously gaseous, no solid substance being formed.

Many substances commonly called incombustible because they do not burn readily in ordinary air, burn vigorously in oxygen. Of these, me-

Fig. 4.

tallic iron may be taken as an example. A watch-spring, which has been rendered flexible by igniting it and allowing it to cool slowly, is made into a spiral coil, and to the end is attached a bit of tinder or of twine soaked in sulphur. If the kindling-material be lighted, and the spiral then plunged into a jar of oxygen, the iron will burn brilliantly with scintillation. From time to time, glowing balls of molten matter fall off from the wire, and bury themselves in the layer of sand which should have been placed at the bottom of the bottle.

14. It is thus clearly proved that iron, when red-hot, combines with oxygen. It is the burnt or **oxidized** iron which falls in globules to the bottom of the bottle. The compounds which are formed by the union of oxygen with other elements are called **oxides.** The substances which have been heretofore mentioned

under the more familiar name of **rust,** like iron-rust, tin-rust, mercury-rust, are called, in chemistry, **oxides ;** as iron oxide, tin oxide, mercury oxide.

15. The most important quality of oxygen is, that, with a single exception, it unites with all the other elements to form compounds which are sometimes solid, as in the case of iron, and sometimes gaseous, as in the case of sulphur (**Exp. 5**). Oxygen is the most widely diffused and the most abundant of all known substances. Not only does it constitute about one-fifth the volume of the air, but at least one-third of the solid crust of the globe is composed of it. It is the chief ingredient of water, as will appear in a subsequent chapter. Silica, in all its varieties of sand, flint, quartz, rock-crystal, etc., contains about half its weight of oxygen ; and the same is true of the various kinds of clay, and of chalk, limestone and marble. It enters largely into the composition of plants and animals, and is absolutely essential to the maintenance of animal and vegetable life.

16. The combination of oxygen with various substances is often accompanied by the development of light and heat, as in **Exps. 5** and **6.** All the ordinary phenomena of fire and light which we daily witness depend upon the union of the body burned with the oxygen of the air. Indeed, the term **combustion** may, for all ordinary purposes, be regarded as synonymous with **oxidation.**

CHAPTER III.

NITROGEN.

17. The simplest method of preparing **nitrogen** is to burn out the oxygen from a confined portion of air, by phosphorus or by a jet of hydrogen.

Exp. 7. — Into a small porcelain capsule, supported on a piece of stout iron wire bent as represented in Fig. 5, put about a cubic centimetre of phosphorus, and set it on fire. Invert over the capsule a wide-mouthed bottle, of the capacity of a litre or more, and hold this bottle so that its mouth shall dip beneath the surface of the water. During the first moments of the combustion, the heat developed thereby will cause the air within the bottle to expand to such an extent, that a few bubbles of the air will be expelled; but, after several seconds, water will rise into the bottle to take the place of the oxygen, which has united with the phosphorus.

Fig. 5.

The dense white cloud which fills the bottle at first is a compound of phosphorus and oxygen, which is soluble in water. It will, therefore, soon be absorbed by the water in the pan, and will disappear; so that at the close of the experiment nearly pure nitrogen will be left in the bottle. But, as the phosphorus ceases to burn before the last traces of oxygen are exhausted, the nitrogen obtained by this method is never absolutely pure.

Remove the wire with the capsule, which may be readily done by tipping the bottle to one side, taking care that the mouth does not come out of the water, and slip a glass plate under the mouth of the bottle; invert the bottle so that it stands upright, and thrust a burning splinter of wood or a lighted candle into the gas; it will be instantly extinguished.

Nitrogen may also be prepared by passing a slow stream of air over bright copper-turnings heated to redness in a hard glass tube. The copper combines with the oxygen of the air, and retains it; while the nitrogen escapes from the tube, and may be collected over water.

18. **Nitrogen** is a transparent, colorless, tasteless, odorless gas, not quite as heavy as air. In its chemical deportment towards other substances, it is remarkably unlike oxygen. Whilst oxygen is active and, as it were, aggressive, nitrogen, at least when in the condition in which it exists in air, is remarkably inert and indifferent as regards entering into combination with other bodies. It is marked rather by the absence of salient characteristics than by any active properties of its own.

As it extinguishes flames, so it destroys life. Animals can not live in an atmosphere of pure nitrogen. It is not poisonous; if it were, it could not be breathed in such large quantities as it is in air. An animal immersed in it dies simply from want of oxygen.

Nitrogen is widely diffused in nature. Besides occurring in the air, it is a constituent part of all animals and vegetables, and of many of the products resulting from their decomposition. Notwithstanding the indisposition of nitrogen in the free state to enter into combination, a very large number of interesting and important compounds can be formed by resorting to indirect methods of effecting its union with other elements.

CHAPTER IV.

WATER.

19. Another natural substance, quite as common as air, is **water.** Three-fourths of the earth's surface is covered with it. It is diffused through the atmosphere in the form of vapor, and is a constituent of all animal and vegetable substances and of many minerals. We take up next this familiar substance, in order that we may gain, through the study of it, a deeper insight into chemical principles, and enlarge our experience by making acquaintance with a new element.

20. At the ordinary temperature of the air, pure water is a transparent liquid, devoid of taste or smell. In thin layers, it appears to be colorless; but large masses of it are distinctly blue, as seen in mid-ocean, in many deep lakes of pure water, and in masses of ice, such as icebergs and some glaciers, where it is possible to look through the ice from below.

21. At 4°, the temperature at which it is densest, water is 773 times heavier than air at 0°. A cubic centimetre of water, at this temperature, weighed in a vacuum, is our unit of weight,

— a **gramme**; therefore, one litre of water, which measures 1,000 cubic centimetres, weighs a kilogramme.

Pure water at 4°, the temperature of its greatest density, is taken as a standard to which the weights of equal bulks of other substances, liquid or solid, are referred. In other words, the **specific gravity** of water is taken as 1; and in terms of this unit the specific gravities of all other liquid and solid substances are expressed. The specific gravity of gold, for example, is 19.3; that is to say, the weights of equal bulks of water and of gold are to one another as 1 to 19.3.

22. When exposed to a certain degree of cold, water **crystallizes** with formation of ice, or snow, according to circumstances; and, upon being heated sufficiently, it is transformed into an invisible gas, called **steam**. Both these changes, however, are purely physical: the chemical composition of the water is the same, whether it be liquid, solid or gaseous. The temperature at which ice melts is one of the fixed points of the centigrade thermometer, numbered 0°, and the temperature at which water boils, under a pressure of 760 m. m. of mercury, is the other fixed point, numbered 100°. Water evaporates at all temperatures, and is therefore a constant ingredient of the atmosphere. Even ice slowly evaporates, at temperatures far below 0°, without first passing into the liquid condition.

In crystallizing, that is to say, in assuming the solid form, water increases in volume. From this fact result many familiar phenomena, such as the floating of ice, the upheaving and disintegrating action of frost, and the bursting of pipes and other hollow vessels, when water is frozen in them.

Steam is a colorless, transparent gas, as invisible as atmospheric air, and considerably lighter than it. When steam escapes into the air, it is partly condensed to the liquid state and there is formed a multitude of little globules precisely similar to the minute drops of water which make up ordinary clouds and fogs. This steam-cloud is sometimes improperly spoken of as steam or vapor, an error against which the student should be on his guard. Similar fogs are formed whenever the atmosphere is

cooled to a temperature so low that the aqueous vapor contained in it can no longer exist in the gaseous state.

Water conducts heat very slowly; it may even be boiled for many minutes at the top of a test-tube, while the lower end of the tube is held in the fingers without inconvenience.

23. Let us now pass to the **analysis** of water. Of what is water composed? We can determine this point by methods similar to those which were adopted in the examination of air. At a low red heat water can be decomposed by several of the metals, such as iron, tin, zinc and magnesium. **Iron** is well adapted for this purpose.

If water be boiled in a suitable flask, and the steam passed through an iron tube (a piece of iron gas-pipe answers very well) filled with bright iron-turnings, and heated red-hot, the steam is decomposed; a gas escapes from the tube, and may be collected over water. On the application of a match, the gas will burn with a pale blue flame. This gas is one of the constituents of water, and is called **hydrogen**. If, after the tube has become cold, the iron-turnings be removed, they will be found to be covered with a black coating similar to that which forms on iron heated in the air.

24. There are certain metals which are capable of decomposing water without the application of heat. The metal **sodium** possesses this power.

Exp. 8. — Make a small cylinder of wire-gauze, by rolling a piece of fine gauze, about 6 c. m. square, around a thick piece of No. 6 glass tubing. Twist fine wire around the cylinder, in order to preserve its form; then slip the cylinder off the glass, and close one end of it by pressure with a stout pair of pincers. Within this cylinder of wire-gauze place a piece of metallic sodium as large as a pea, and then close the upper end of the cylinder by pressure with the pincers, as before.

Attach the wire-gauze cage firmly to the end of a piece of stout iron wire and thrust it quickly into the water-pan, so that the cage will come directly under the mouth of a small bottle of about 100 c. c. capacity, which has been previously filled with water, and is held inverted in the pan (Fig. 6).

Fig. 6.

As soon as the water comes in contact with the sodium, bubbles of gas will begin to escape from the wire-gauze cage, and, passing up through the water, will collect at the top of the inverted bottle. When the evolution of gas has ceased, close the mouth of the bottle with a small plate of glass, turn the bottle mouth uppermost, remove the plate, and touch a lighted match to the gas. The gas will take fire with a sudden flash. The gas is **hydrogen**; the sodium has united with the other constituent (or constituents) of the portion of water decomposed, and the new compound formed is dissolved by the water in the pan.

25. By these experiments it has been proved that one of the components of water is a gas called **hydrogen**. But, with the exception of the coating upon the iron alluded to in **§ 23,** we have as yet nothing to indicate what other ingredients the water may contain. Such evidence can, however, be readily obtained by resorting to another method of analysis.

If a galvanic current is caused to flow through water, the force by which the constituents of the water are held together will be overcome, and the water will be resolved into the elements of which it is composed. On immersing the platinum poles of a galvanic battery in water, to which a little sulphuric acid has been added for the purpose of increasing its conducting power, minute bubbles of gas will immediately be given off from these poles, and will be seen rising through the liquid. If the apparatus be so arranged that we can collect the gas given off from each pole in a test-tube filled with water to which a little sulphuric acid has been added, it will be found that twice as much gas has collected in the one tube as in the other. If the test-tube containing the larger volume of gas be now closed with the thumb, turned mouth uppermost, and the gas within touched with a lighted match, it will take fire and burn with the characteristic flame of hydrogen. It is, in fact, **hydrogen**. If the smaller volume of gas in the other tube be examined in the same way, it will not inflame, although it gives intense brilliancy to the combustion of the match. If a splinter of wood, retaining but a single ignited spark, be

Fig. 7.

immersed in the gas, it instantly exhibits a vivid incandescence, and in a moment bursts into flame. This gas is **oxygen**.

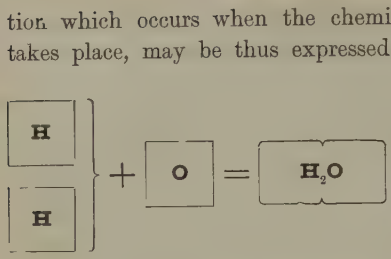
It is thus proved, that out of water may be unloosed two volumes of hydrogen, and one volume of oxygen. It remains to see whether we can produce water from a mixture of oxygen and hydrogen. If we introduce into a stout test-tube a mixture of two volumes of hydrogen and one volume of oxygen, on touching a lighted match to the mixed gas it instantly explodes with great violence, the hydrogen burning suddenly, so that for a moment a flash of flame fills the whole interior of the tube. After the explosion, water will be found deposited as dew upon the inner walls of the tube.

26. We have thus established the composition of water by **analysis,** having resolved water into two gaseous constituents, **hydrogen** and **oxygen ;** we have also proved, by the converse or **synthetical** method, that hydrogen and oxygen are its only constituents, since we have reproduced water by effecting the chemical union of these two elementary materials mixed in due proportion.

This proportion is fixed and invariable ; pure water is always made up of hydrogen and oxygen in the proportion of two volumes of the former for one of the latter. From the known specific gravities of the two gases, as well as by direct experiment, the composition of water *by weight* has been found to be 1 part by weight of hydrogen to 8 parts by weight of oxygen. This proportion is also constant and it is in general true that,—*Any given chemical compound always contains the same elements combined in the same proportions.* This is the **Law of Definite Proportions.**

There is one important point still to be considered. If the union of the elements be effected in an apparatus so arranged that the water, when formed, is kept at such a high temperature that it remains in the gaseous condition under which it is known as **dry steam,** we find that the two volumes of hydrogen and one volume of oxygen which were mixed together have, by uniting chemically, become compacted into two volumes of steam. If equal volumes of hydrogen and oxygen be represented by equal squares, having the initials of the elements inscribed therein, the composition of water by volume, and the condensa-

tion which occurs when the chemical union of the elements takes place, may be thus expressed to the eye :



Each smallest possible or greatest conceivable volume of steam will invariably yield, on decomposition, its own volume of hydrogen, and half its volume of oxygen.

27. It has been agreed among chemists to call by the name **molecule** the least quantity of a compound, or of an elementary substance which can exist by itself uncombined, or take part in any chemical process. The smallest conceivable portion of water (which by this definition is called the molecule) like any larger quantity of water, is made up of hydrogen and oxygen, and if decomposed would yield twice as large a volume of hydrogen as of oxygen. The smaller masses of matter which make up the molecules are called **atoms**. The term **atom** may be defined as the smallest quantity of an element which can be conceived to exist in combination. A molecule, as a rule, contains more than one atom, and may contain a great number; these atoms may be all of one kind, in which case the molecule is that of a simple substance, or they may be of several kinds, as in the molecules of compound substances.

There is good reason to believe that equal volumes of the elementary gases, oxygen and hydrogen (also nitrogen and chlorine to be studied hereafter) contain the same number of atoms. (See § **140**.) If this be true there will be in the molecule of water twice as many atoms of hydrogen as of oxygen, because when any quantity of water whatever is decomposed, it yields twice as much hydrogen by volume as oxygen. The symbol H_2O, which has been already used to indicate the *volumetric* composition of water (§ **26**), may also be used to indicate the *atomic* composition ; the H_2 will represent two *atoms* of hydrogen, the O an *atom* of oxygen, and the H_2O a *molecule* of water.

28. It must be distinctly borne in mind that as to the abso-

lute size of the atoms, we know nothing; the same thing is true with regard to their absolute weight. It is, however, not difficult to determine their relative weight. If we take the case of hydrogen and oxygen, any given bulk of oxygen weighs 16 times as much as the same bulk of hydrogen, and as there are the same number of atoms in equal bulks of these two gases, the single atom of oxygen must weigh 16 times as much as the single atom of hydrogen. The numbers 1 and 16 are called the **atomic weights** of hydrogen and oxygen, respectively, and it is possible, although not always by the same method, to determine the relative weights of the atoms of all the elements. The atomic weight is, in each case, referred to that of hydrogen, which is called 1.

If the atomic weights of hydrogen and oxygen be borne in mind, the symbol of water, H_2O, will now remind us of the composition of water *by weight*, for as each molecule of water is made up of two atoms of hydrogen and one atom of oxygen, the proportion by weight in which these two elements are combined together will be as 2 to 16, or as 1 to 8.

29. Having thus succeeded in determining the constituents of air and **water,** we are naturally led to inquire whether it be not possible to resolve oxygen, nitrogen and hydrogen themselves into simpler forms of matter. To this question but one answer can be made, namely, that oxygen, nitrogen and hydrogen are incapable of decomposition by any means as yet at our disposal. We are, therefore, justified in regarding these gases as *simple* bodies, or **elements,** in contradistinction to decomposable bodies, such as air and water.

30. The **water** which occurs in nature is never absolutely pure. In the form of ice, and as it falls from the clouds as rain or snow, it is, indeed, tolerably free from foreign substances; but, after having once soaked into the ground, it becomes charged with a variety of mineral and other substances, which, being soluble in water, are dissolved by it as it trickles through the earth.

Where the proportion of soluble matter contained in the water

is unusually large, and particularly if it possesses marked medicinal properties, the water is called mineral water, and the springs from which it issues are known as mineral springs. Sea-water may be regarded as a variety of mineral water.

31. For the conduct of chemical investigations, it is often necessary to purify natural water. This is done by a process called **distillation.** As a general rule, distilled water is employed in all delicate chemical operations.

Exp. 9. — In a retort of 500 c. c. capacity, put 200 or 300 c. c. of well-water. Thrust the neck of the retort into a half-litre receiver placed in a pan of cold water. Cover the receiver with a cloth or with coarse paper, and upon this pour cold water from time to time, or pile upon it fragments of ice. Place the retort upon wire-gauze, on a ring of the iron lamp-stand, and adjust the distance of the retort from the lamp as described in Exp. 3, Fig. 2. Light the lamp beneath the retort, and bring the water to boiling. As fast as the water in the retort is converted into steam, this vapor will pass over into the cold receiver, and will there be condensed again to the liquid condition. Continue to boil until about three-quarters of the water in the retort has evaporated.

Fig. 8.

The earthy and saline ingredients of well-water are for the most part not volatile : very few of them are capable of accompanying the water as it goes off in vapor ; hence the greater part of the original impurity of the water will remain behind in the retort.

Exp. 9 a. — Place a few drops of the distilled water obtained in the preceding experiment upon a piece of platinum-foil (Appendix, § 14). Hold the foil with iron pincers above the gas-flame in such a manner that the liquid may slowly evaporate without boiling or spirting. After the water has disappeared, no residue will be found upon the foil. Take now the same number of drops of water from out the retort, and evaporate them upon the foil as before. A very decided residue of earthy matter will be left upon the foil.

32. In the operation of **distillation,** the substance to be distilled must in the first place be converted into the condition

of vapor; this vapor must next be transferred to another vessel, and there, by refrigeration, be again condensed to the liquid state. As will appear from the foregoing experiment, the vaporization is effected in the **retort** or **still**, and the refrigeration in the **condenser**. In the experiment above given, the receiver acts at once as receiver and condenser; but in many cases it is better to interpose a cooling-apparatus between the retort and the receiver. A convenient form of such apparatus, known as **Liebig's condenser**, is arranged so that the vapor to be condensed must pass into a long tube which is kept cool by being enclosed in a larger tube through which cold water is made to circulate. A figure representing such a condenser will be found on page 146.

33. The mineral and other substances alluded to above are not the only impurities of natural water. It contains also oxygen and nitrogen in solution, as both of these gases, which are present in the air, are somewhat soluble in water. That water does actually contain dissolved gases may be shown by the following experiment.

Exp. 10. — By means of a sound perforated cork or caoutchouc stopper, adapt to a flask of the capacity of 1 or 2 litres a gas-delivery tube, No. 6, long enough to reach to the water-pan in the usual way. Upon the outer end of the delivery-tube tie a short piece of caoutchouc tubing, to which a stopper made of a bit of glass rod, or a wooden plug, has been fitted. Fill the flask completely with ordinary well or river water; fill also the delivery-tube with water, and close it by putting the stopper in the caoutchouc tube. Carefully place the cork of the delivery-tube in the neck of the flask in such manner that no air shall be entangled by the cork; at the same moment remove the plug from the delivery-tube, and finally press the cork firmly into the flask. Both flask and tube will now be completely full of water. Place the dried flask upon a ring of the iron stand, and invert a bottle filled with water over the end of the delivery-tube. Now slowly bring the contents of the flask to boiling.

As the water gradually becomes warm, numerous little bubbles of gas will be seen to separate from the liquid, and to collect upon the sides of the flask; these subsequently coalesce to larger bubbles, which collect in the neck of the flask. As soon as the water actually

boils, the steam will force this gas out of the flask, and it will collect in the inverted bottle at the end of the delivery-tube, the steam being meanwhile condensed as fast as it comes in contact with the cold water in the pan. By continuing to boil moderately during ten or fifteen minutes, nearly all the gas can be swept out from the flask by means of the escaping steam. The delivery-tube may then be lifted from the water-pan and the lamp extinguished. As to the exact character of the gases thus collected we shall learn something in a subsequent chapter.

34. As might be inferred from the foregoing, water has the property of dissolving many substances, solid, liquid and gaseous. Sugar, for example, dissolves readily in water; but sand is insoluble therein. A substance is said to be **soluble** in water when it is capable of being divided in and dispersed through the water so intimately and completely that its particles become invisible, and can no longer be separated by filtration; the result of this coalescence, or the **solution** as it is termed, is a transparent liquid, as a general rule scarcely less mobile than the water itself.

Of the various substances soluble in water, some dissolve in far larger proportion than others. With some liquids, as alcohol for example, water can be mixed in any proportion; but of ether it dissolves but little, and of oil none. The proportion of any substance that can be dissolved in a given quantity of water is usually limited, and, under fixed conditions, is definite and peculiar for each substance. When a given quantity of water has dissolved as much of a substance as it is capable of dissolving at the temperature and pressure to which it happens to be exposed, the solution is said to be **saturated.** Of nearly all solid substances, hot water dissolves a greater quantity than cold water: gases, however, are less soluble in hot than in cold water, as already illustrated by **Exp. 10.**

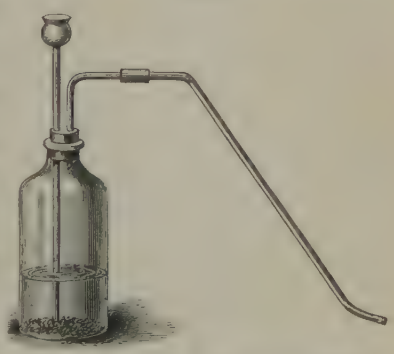
CHAPTER V.

HYDROGEN.

35. The commonest method of preparing **hydrogen** is by treating zinc or iron with sulphuric or muriatic acid. Unless very large quantities of the gas are needed, this method is much more convenient than either of those heretofore mentioned.

Exp. 11. — To a bottle 18 or 20 c. m. high, and of 500 or 600 c. c. capacity, the mouth of which has an internal diameter of 2.5 to 3 c. m., fit a caoutchouc stopper or a sound cork, furnished with a thistle-tube, Fig. 9, and a gas delivery-tube, of No. 6 glass. Within the bottle put 15 or 20 grms. of granulated zinc, or small scraps of the sheet metal, and as much water as will fill about one-quarter of the bottle. Replace the cork in the bottle, taking care to press it in tightly, and gradually pour in common muriatic acid through the thistle-tube. The thistle-tube must reach nearly to the bottom of the bottle, so that its point may dip beneath the water; and the muriatic acid must be added by small successive portions, — not more than a large thimbleful at a time.

Fig. 9.



On the addition of the first portions of the acid, chemical action will ensue, the contents of the bottle will become warm, and gas will be seen to escape from the liquid. This gas is hydrogen.

After all the air has been expelled from the bottle, the hydrogen may be collected over the water-pan, in inverted bottles filled with water. The moment at which the hydrogen ceases to be contaminated with air can be determined by collecting small portions of the escaping gas in wide-mouthed bottles of about 50 c. c. capacity, and testing its quality by means of a lighted match. In doing this the small

bottle filled with gas must not be turned over, but should be carefully lifted from the water without changing its vertical position, and the lighted match should then be applied to the mouth of the bottle. If the hydrogen be pure, it will burn tranquilly at the mouth of and within the bottle ; but, in case the gas is still mixed with much air, a sharp explosion will occur at the moment when the match is touched to it. In experimenting with hydrogen, no light should ever be brought into contact with the contents of the bottle in which it is generated, or with any large quantity of the gas, until the purity of the sample, or rather its non-explosive character, has been demonstrated by applying to a very small volume of the gas the test above described.

This experiment, which has here been executed with zinc, can be equally well performed with iron-filings, and with several other of the less common metals.

36. We now proceed to study the chemical action which takes place in the above experiment. The muriatic acid, or, in chemical language, **chlorhydric acid**, which was employed, is, in reality, a solution in water of a very soluble gaseous substance, to which the name chlorhydric acid is more strictly applied. This gaseous substance, the pure chlorhydric acid, is a chemical compound of the element hydrogen and of another element, called **chlorine**, which will shortly be described. The compound may be represented by the symbol **HCl**, in which **H** represents, as before, the least proportional weight of hydrogen which exists in combination, and **Cl** the least proportional weight of chlorine. We may likewise abbreviate the word **zinc** to the symbol **Zn**; and the chemical process, or **reaction**, by which the hydrogen is liberated, may then be symbolized by the *equation*, —

$$2\,HCl + Zn = ZnCl_2 + 2\,H.$$

Since hydrogen is gas, it escapes as such, and there remains dissolved in the water within the bottle a compound of the elements chlorine and zinc, called **zinc chloride**. The zinc, which was free, enters into combination, and the hydrogen, which was in combination, is set free ; in other words, the zinc has been **substituted** for, or has **replaced**, the hydrogen.

It may here be stated that chemists of all nations have agreed to represent each of the elements by a symbol which consists either of the initial letter of the Latin name of the element, or, when the names of two or more of the elements begin with the same letter, of the initial letter, together with the first of the succeeding letters in the Latin name, which is distinctive. Thus **Fe** (*Ferrum*) is the symbol of iron, **C** of carbon, **Ca** of calcium, **Cl** of chlorine, and **Cr** of chromium. These symbols do not serve simply as abbreviations, but each stands for *a single atom* of the element indicated; if we know the atomic weight of the element, the symbol may stand to us also for a *certain definite weight* of the element in question, as we have seen in § 26. In the same section the symbols **O** and **H** were used to indicate *one volume* of oxygen and hydrogen, respectively: this use of the symbols to express volumetric relations is, however, not the same for all the elements, and it will be treated of in Chapter XI.

A group of these elementary symbols just described, written together, stands for a molecule made up of the atoms indicated. Thus **HCl** stands for a molecule containing one atom of hydrogen and one atom of chlorine; $\mathbf{ZnCl_2}$ stands for a molecule made up of one atom of zinc and two atoms of chlorine; the figure 2 written *below the line* applies to the **Cl** alone. If the figure 2 were written *on the line*, and before the symbol, it would indicate two molecules of the compound; as **2 HCl**. The knowledge of the atomic weights enables us to use the molecular symbols to express the composition of a substance by weight; thus we have already seen (§ 26) that $\mathbf{H_2O}$ indicates that in every 18 parts by weight of water there are 16 parts by weight of oxygen, and 2 parts by weight of hydrogen. In the same way, knowing the atomic weight of chlorine to be 35.5, from the symbol **HCl** we learn that in every 36.5 parts by weight of chlorhydric acid there are 35.5 parts by weight of chlorine, and 1 part by weight of hydrogen. We say the **molecular weight** of water is 18, and the molecular weight of chlorhydric acid is 36.5, meaning that the molecule of water weighs 18 times, and the molecule of chlorhydric acid 36.5 times as much as the atom of hydrogen, which is taken as the unit of molecular as well as of atomic weight. The circumstances under which we may also learn the *volumetric* composition of a compound from the symbol of its molecule, will be discussed hereafter. (See page 291.)

Every well-understood chemical action may be expressed as an *equation*. The one just given, $\mathbf{2\,HCl + Zn = ZnCl_2 + 2H}$,

indicates that from the action of 2 molecules of chlorhydric acid and 1 atom of zinc upon each other, there result 1 molecule of zinc chloride and 2 atoms of hydrogen. Of course, as the experiment was actually performed, a vast number of molecules of chlorhydric acid, and the corresponding number of atoms of zinc, acted upon each other,—the equation indicates merely the *relative* number. It follows naturally from the very conception of atoms and molecules, that whenever chemical action takes place between two bodies, it is always between fixed and definite weights of those two bodies. Our knowledge of the atomic weights of the various elements, enables us to calculate from the equation what must be the relative proportion by weight of the substances concerned in the action. The atomic weight of zinc is 65, and the molecular weight of chlorhydric acid is 36.5, and the equation shows us that for every atom of zinc weighing 65 of our units of weight (the unit being the weight of an atom of hydrogen), two molecules of chlorhydric acid must be taken which weigh 73 (*i. e.*, 2×36.5) of these same units: moreover, from the action on each other of these amounts of zinc and chlorhydric acid, there are formed one molecule of zinc chloride, weighing 136 (*i. e.*, $65 + 71$), and two atoms of hydrogen weighing 2 of these same units. It is, of course, immaterial whether the unit of weight be the weight of an atom of hydrogen, or a pound, or a kilogramme; the relative proportion, according to which these two substances act upon each other, must in every case be the same, and the following proportions will hold true:—

$$\left\{\begin{matrix}\text{Weight of zinc}\\ \text{in any case}\end{matrix}\right\} : \left\{\begin{matrix}\text{Weight of } \mathbf{HCl}\\ \text{in same case}\end{matrix}\right\} = 65 : 73.$$

$$\left\{\begin{matrix}\text{Weight of zinc}\\ \text{in any case}\end{matrix}\right\} : \left\{\begin{matrix}\text{Weight of } \mathbf{ZnCl_2}\\ \text{in same case}\end{matrix}\right\} = 65 : 136.$$

If the weight of zinc used in any case were given, the weight of chlorhydric acid required could be readily calculated, as we should then have three terms of a proportion given to find the fourth; moreover, the amount of zinc chloride produced by the use of 65 parts of zinc would be $65 + (2 \times 35.5)$, that is, 136 parts by weight. In fact, if the amount of any one of the four substances were given, the amounts of the other three could be found, as they are all proportional. (See also §§ 63 and 76.)

It is also to be remarked that, in writing the equation, no account was taken of the water in which the **HCl** was dissolved. This water

remained in the bottle unchanged after the experiment was finished, and in it the zinc chloride ($ZnCl_2$) formed was held in solution. It would be possible by the application of heat to evaporate all of this water and leave the zinc chloride as a solid substance.

37. **Hydrogen** is a transparent, colorless and tasteless gas, odorless when pure. It is not poisonous, though animals die from suffocation when immersed in it, as they do in an atmosphere of nitrogen. It is the lightest substance known; being about $14\frac{1}{2}$ times lighter than air, 11,160 times lighter than water, and 151,700 times lighter than quicksilver. Hydrogen is the standard of **specific gravity** for gases, as water is for liquids and solids; its specific gravity is therefore unity.

38. The exceeding **lightness** of hydrogen can be illustrated by filling soap-bubbles with the gas. They will rise rapidly through the air; and, if touched with a lighted taper, the hydrogen will immediately burst into flame. Owing to its lightness hydrogen can readily be poured or decanted upwards from one vessel to another.

Exp. 12. — Lift from the water-pan a thick, strong, wide-mouthed bottle, of 200 to 300 c. c. capacity, full of hydrogen, taking care to hold it in a perpendicular position, with the mouth downward. With the other hand place another bottle of equal size and strength, but containing only air, beside the hydrogen-bottle, so that the mouths of the bottles shall touch at one edge. Gradually turn down the hydrogen-bottle, and at the same time push its mouth beneath that of the air-bottle in such manner that the bottle which originally contained the hydrogen shall at last stand upright beneath the inverted bottle. During this operation, the lighter hydrogen flows up into the upper bottle, while the heavier air sinks into the lower. If a burning match be now thrust into the upper bottle, the hydrogen within it will take fire; but, upon applying the match to the lower bottle, originally full of hydrogen, there will be found in it nothing but air.

Since hydrogen is thus lighter than air, it is not absolutely necessary, in collecting it, to operate over water, as has been directed. When a gas is much lighter or heavier than atmospheric air, it may often be conveniently collected by **displacement**. A bottle can be readily filled with hydrogen from a gas-holder by carrying the delivery-

tube to the top of the inverted bottle, and allowing the gas to flow in. After a short time the air will be wholly displaced, and the bottle filled with hydrogen.

39. There is another noticeable peculiarity of hydrogen which is directly connected with its extreme lightness. It possesses in a high degree the power of **diffusion.** This diffusive power is a physical property common to all gases and vapors; in the case of hydrogen, it is only the intensity of the diffusive power which is remarkable. The following experiment will serve to illustrate this property.

Exp. 13. — A glass tube, 3 or 4 c. m. in diameter, and 30 or 40 c. m. long, is closed at one end with a plug of plaster of Paris 1 or 2 c. m. thick. The tube is then set aside for a day or two, in order that the plaster may become dry. When the plug is dry, fill the tube with hydrogen by displacement, and set it upright in a glass of water. Water will rise rapidly in the tube, since hydrogen escapes through the plaster more rapidly than air can enter the tube through this porous plug. If the tube be left to itself, air will slowly enter through the plaster, so that the water within the tube will in due time sink to the level of the outside liquid.

Fig. 10.

The velocities with which gases diffuse are in the inverse ratio of the square roots of their specific gravities. Hence it happens that hydrogen, being the most attenuated of all gases, diffuses with the greatest rapidity. Compared with that of oxygen, its rate of diffusion is as 4 to 1; that is to say, the relative rates of diffusion of the two gases are inversely as the square roots of the numbers 1 and 16, which represent the specific gravities of hydrogen and oxygen respectively.

On account of its high diffusive power, hydrogen can be kept only in perfectly tight vessels. It can not be kept for any length of time in bladders or rubber bags, and it will leak through stopcocks which are perfectly tight for nitrogen or oxygen.

40. **Hydrogen** is exceedingly inflammable, as has been already seen; that is to say, the temperature at which it takes fire is comparatively low. But, as a matter of course, it extinguishes

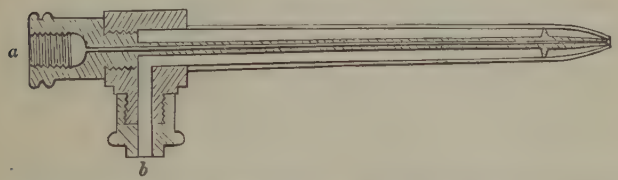
any burning body which is immersed in it, since oxygen is necessary for the support of combustion.

Exp. 14. — Carefully lift from the water-pan a bottle of 200 or 300 c. c. capacity, completely full of hydrogen ; slowly carry the bottle, the mouth of which is, of course, held downward, to a burning candle or splinter of wood, and depress the bottle over this flame. The hydrogen will take fire and burn below, at the mouth of the bottle, where it is in contact with the oxygen of the atmosphere ; but the flame of the candle will be extinguished the moment it becomes completely enveloped by the hydrogen. The candle can easily be relighted by slowly lifting the bottle until the wick is brought into contact with the air and the burning hydrogen.

Fig. 11.

41. It has been seen that the **hydrogen flame** gives but very little **light** ; it is, however, very **hot.** Indeed, it has been found that when a given weight of hydrogen enters into chemical union with oxygen, more **heat** is developed than in the burning of the same weight of any other substance. On this fact depends the use of the so-called **oxy-hydrogen blowpipe.**

Fig. 12.



The principle of the construction of this apparatus may be learned from Fig. 12. It consists essentially of two tubes, one within the other. The inner tube (*a*) is connected with a gas-holder containing oxygen ; the outer tube (*b*) with a gas-holder containing hydrogen. The cock of the hydrogen gas-holder is first opened and the hydrogen is lighted at the point of the jet ; the cock of the oxygen gas-holder is then slowly opened until the flame is reduced to a fine pencil. A constant and sufficient pressure should be maintained on the gas-holders.

In the flame thus produced, a fine platinum wire will readily melt and fall into drops. The intense heat of the oxy-hydrogen flame is thus admirably illustrated, for platinum is an exceedingly infusible metal, which can scarcely be softened in the hottest furnace.

If a piece of chalk or lime, scraped to a fine point, be held in the flame of the oxy-hydrogen blow-pipe, it will quickly become white-hot, and evolve light of great brilliancy, almost comparable with that of the sun. On this principle is constructed the so-called Drummond or calcium light, often employed for night-signals and optical experiments.

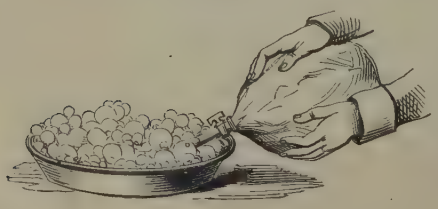
42. No matter in what way **hydrogen** is burned, whether in the pure state or in combination with other materials, whether in pure oxygen or in the air, the **product** of the combustion is always **water.** At the high temperature of the flame, this water must, of course, remain in the condition of a gas, but it can readily be brought to the liquid state by reducing the temperature.

Exp. 15. — Over a jet of burning hydrogen, best obtained from a gas-holder, hold a dry, cold bottle. The glass soon becomes covered with a film of dew, as the water generated by the union of hydrogen and oxygen condenses in droplets upon the cold sides of the bottle.

43. If, instead of burning pure hydrogen as it flows into the air, the gas be first mixed with oxygen, and then ignited, a very different result will be obtained. The hydrogen being now in contact with oxygen at all points, the entire mass of gas will burn with a violent explosion at the instant when a light is touched to it.

This may be illustrated by connecting a piece of glass tubing with a gas-holder, or, better, a rubber bag, containing a mixture of 2 volumes of hydrogen and 1 volume of oxygen. The end of the glass tube is dipped into a dish of soap-suds, and the gas allowed to flow until a

Fig. 13.



mass of foam not too large has formed on the surface of the suds. If, after the removal of the gas-holder, the foam be touched with a long lighted stick, a violent explosion will occur.

Care should be taken to throw away any remnant of the mixture of hydrogen and oxygen which may have been left in the gas-holder at the close of the experiment, and upon no account should fire ever be brought into its vicinity.

The loud explosion is owing to the fact that the intense heat emitted at the moment of the combination of the two gases expands enormously the steam formed by their union. As the steam is immediately condensed, there results a partial vacuum, into which air rushes from all sides; and it is the heavy and sudden undulations thus communicated to the air which occasion the noise. The outward and inward shocks follow one another so quickly that the ear cannot distinguish between them.

44. Mixtures of hydrogen and air produce less violent explosions than mixtures of hydrogen and oxygen, because of the inert nitrogen in the air, which acts as an elastic pad or cushion to break the force of the shock.

Exp. 16. — Introduce 2 volumes of hydrogen and 5 volumes of air into a strong round-bottomed bottle, such as is used for soda-water. Close the mouth of the bottle with a cork, and shake violently, in order that the gases shall be mixed. A small quantity of water should be left in the bottle to act as a stirrer. Grasp the bottle firmly in one hand, remove the cork with the other, and apply the open mouth of the bottle to a lighted candle. An explosion will immediately ensue.

45. Since air is everywhere about us, and since all ordinary combustions occur in it, it has become customary to speak of it and of oxygen as **supporters of combustion,** in contradistinction to the so-called **combustibles,** such as hydrogen. These terms are often convenient; but that they have only a relative, and no absolute significance, may be shown experimentally, as follows: —

Support a rather wide tube of thin glass — the neck of a broken retort, for example — in a vertical position, and connect the upper opening with a gas-holder containing hydrogen. Allow the gas to flow until the tube is filled; then apply a lighted match to the mouth of the tube, and regulate the flow of gas so that the latter may continue to burn slowly at the lower edge of the tube.

Fig. 14.

With a second gas-holder containing oxygen, connect a piece of narrow glass tubing, drawn out to a fine point; and, while the oxygen is flowing through this tube, pass it up into the larger tube filled with hydrogen. As the stream of oxygen passes through the burning hydrogen at the bottom of the vertical tube, it takes fire, and afterwards continues to burn in the atmosphere of hydrogen within the tube.

CHAPTER VI.

COMPOUNDS OF NITROGEN.

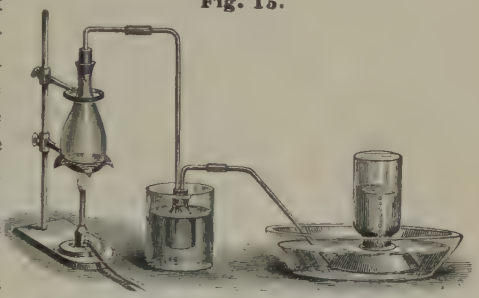
46. We have already learned that nitrogen is, under ordinary conditions, a very inert substance, and indisposed to enter into chemical combination. There are, however, many compounds of nitrogen which either exist in nature, or may be prepared by indirect methods, and the study of the compounds of nitrogen and oxygen will bring to view a new fact of great significance. The study of **water** showed us that in a chemical compound, the elementary constituents are combined in a certain **definite proportion**; we shall now learn that two chemical elements may combine in *more than one* definite proportion to form chemical compounds differing from each other and from the constituent elements.

47. **Nitrous Oxide** (N_2O). — The first compound of nitrogen and oxygen which we shall study may be readily obtained

by gently heating a substance known as **ammonium nitrate**, of which we shall learn more hereafter.

Exp. 17.—Into a *dry* flask of thin glass of about 300 c. c. capacity, introduce 10 or 15 grms. of ammonium nitrate. From the flask placed upon the wire-gauze on the iron stand, carry a delivery-tube, No. 6, beneath the saucer in the water-pan; but interrupt the tube at some convenient point to interpose, by means of a cork or caoutchouc stopper with two holes, a small bottle, which can be kept cool with water, as shown in the figure.

Fig. 15.

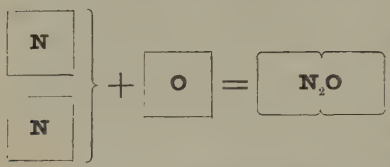


Heat the flask moderately and cautiously, to avoid breaking it. The ammonium nitrate will melt, and little bubbles will soon begin to escape from the fused mass. The heat must now be so controlled that the evolution of the gas shall not be tumultuous. The gas is to be collected in bottles of 300 to 400 c. c. capacity. If the process has been successfully conducted, there will be found in the cooled bottle through which the gas passes, a clear, colorless liquid, which on examination will prove to be water, and nothing else. When one or two bottles of gas have been filled, and enough water for testing has condensed, the delivery-tube may be withdrawn from the water, and the lamp extinguished. The ammonium nitrate might be entirely resolved into water and the gas which now awaits examination; but there is danger of breaking the flask. That the nitrate leaves no residue behind, when sufficiently heated, may be proved by heating a crystal of it on platinum foil over the gas-lamp.

Exp. 18.—Insert a glowing splinter of wood into a bottle of the gas. It will re-inflame with almost as much energy as in oxygen.

48. From the energy with which the glowing splinter bursts into flame, it may be inferred that oxygen is a constituent of the new gas which we have just prepared, and, indeed, repeated experiments have shown that it is composed of the elements

nitrogen and **oxygen**; and that, as in the case of water two volumes of hydrogen and one volume of oxygen are condensed into two volumes of dry steam, so two volumes of nitrogen and one volume of oxygen are here condensed into two volumes of this transparent gas. As the chemical formula or symbol of water is H_2O, so the formula of this new gas is N_2O, and its volumetric composition may be represented by a diagram similar to that by which we conveyed to the eye the composition of water. The gas is called **nitrogen protoxide** or **nitrous oxide.** The equation which represents the chemical action by which it was produced may be thus written:



$$NH_4NO_3 = 2H_2O + N_2O$$

Ammonium nitrate. Nitrous oxide.

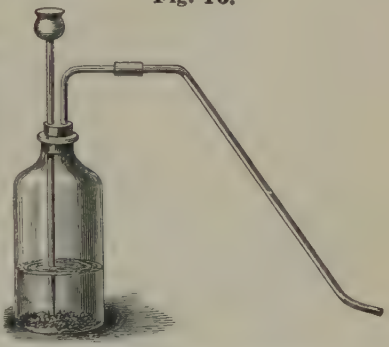
From the above composition by volume, and from the known specific gravities of nitrogen and oxygen, the composition of nitrogen protoxide by weight is readily deduced. The specific gravity of nitrogen, referred to hydrogen, is 14; that of oxygen 16; since there are two volumes of nitrogen for each volume of oxygen, the two elements must, in any given weight of the gas, be combined in the proportion of 28 parts by weight of nitrogen to 16 of oxygen. The molecule of nitrogen protoxide, N_2O, must be composed, like any other quantity of the gas, of 28 parts by weight of nitrogen and 16 of oxygen; but, precisely as in the case of water, we conceive of the molecule as made up of two atoms of nitrogen and one atom of oxygen; and we have already learned that if the atomic weight of hydrogen be represented by 1, that of oxygen must be 16. It follows, from the constitution of nitrogen protoxide, that, if 16 represents the smallest proportional weight of oxygen which exists in combination, 14 must be the corresponding smallest weight of nitrogen when thus united with oxygen. Nitrogen protoxide contains $\frac{16}{44}$, or 36.36 per cent, of oxygen.

49. **Nitrous oxide,** *when pure*, may be respired for a few minutes with impunity. When inhaled, it produces a lively intoxication, attended with a disposition to muscular exertion and violent laughter; whence its trivial name of **laughing gas.** It may, however, be administered so as to cause complete insensibility to pain; the effect lasts, however, for only a very short time. It is advantageously used as an anæsthetic in such surgical operations as can be performed in a few seconds.

50. **Nitric Oxide (NO).**—We now proceed to investigate another compound of nitrogen and oxygen which may be prepared from a chemical substance with which we shall soon be familiar, **nitric acid.**

Exp. 19.—Place 15 or 20 grms. of copper turnings or filings in a bottle arranged precisely as for generating hydrogen (see Experiment 11, § 35), and pour about 25 c. c. of dilute nitric acid made by adding to the common strong acid its own bulk of water. Brisk action will immediately occur. The generator becomes filled with red fumes which gradually disappear, and when the gas disengaged is collected over water, it is found to be colorless. Collect three bottles, of 300 to 400 c. c. capacity of this gas, adding acid from time to time as may be necessary. Save the blue solution (copper nitrate) which remains in the generator for future use.

Fig. 16.

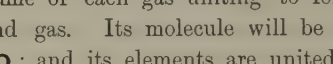


Exp. 19a.—Dip a lighted candle into a bottle of the gas. The light is extinguished. Into the same bottle thrust a glowing splinter. It will not inflame.

Exp. 19b.—Lift a bottle of the gas from the water so that air may enter the bottle, and the gas may escape into the air. Red fumes, of very disagreeable smell, and very irritating when inhaled, are abundantly produced. Bring into contact with these fumes, a piece of moistened *litmus-paper*. It becomes red; the significance of this action will appear later.

Exp. 19c.—Thoroughly ignite a bit of sulphur in a deflagrating-spoon, and introduce it into a bottle of the gas. It will not burn. Into the same bottle thrust a piece of phosphorus as big as a pea, burning *actively*. The combustion will be continued with great brilliancy.

51. By the preceding experiments we learn that the new gas is transparent and colorless, and that it differs notably from all the other gases thus far studied in its relation to combustibles. Analysis shows that the gas consists of **nitrogen** and **oxygen**, one volume of each gas uniting to form two volumes of the compound gas. Its molecule will be represented by the formula **NO**; and its elements are united by weight in the proportion of 14 parts of nitrogen to 16 of oxygen, because equal volumes of nitrogen and oxygen weigh respectively 14 and 16 times as much as the same volume of hydrogen. Its composition may be represented by the accompanying diagram.



The gas is thus another oxide of nitrogen; it is generally known as **nitric oxide**, but some regard the molecule as N_2O_2 and name the compound **nitrogen binoxide**.

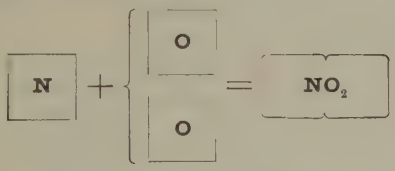
The action of the copper on the nitric acid in **Exp. 19.** may be represented by the following equation:—

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3CuN_2O_6} + 4H_2O + \underset{\text{Nitric oxide.}}{2NO}.$$

When the same element unites with oxygen in more than one proportion, the compound containing a single atom of oxygen in the molecule is called the *protoxide;* when the molecule contains two atoms of oxygen, the compound is called the *binoxide;* succeeding oxygen compounds would be the *teroxide*, *quadroxide*, etc. The term peroxide may be applied to any compound containing more oxygen than the protoxide, although if there are several such oxides it is used conventionally, to denote a particular one. Sometimes the relative amount of oxygen is indicated by the terminations *-ous* and *-ic*; in this case *-ous* implies less oxygen than *-ic*; nitr*ous* oxide contains less oxygen than nitr*ic* oxide. These terminations are not

restricted in their use to oxygen compounds ; we shall, hereafter, meet such terms as ferr*ous chloride* and ferr*ic chloride*, stann*ous sulphide* and stann*ic sulphide*.

52. **Nitrogen peroxide** (NO_2).—The red fumes of **Exp. 19b**, seen when nitric oxide was brought into the air, were due to the chemical union of nitric oxide with oxygen ; a third oxide of nitrogen was formed,—**nitrogen peroxide.** The volumetric composition of nitrogen peroxide will be understood from the accompanying diagram. The molecule will be represented by the formula NO_2, and the composition of the substance by weight will be 14 parts of nitrogen and 32 of oxygen in every 46 parts by weight of nitrogen peroxide.



53. Although at ordinary temperatures nitrogen peroxide is a gas, it can readily be condensed to a liquid. For this purpose, it is best prepared by heating a substance known as lead nitrate.

Exp. 20.—Fill a perfectly dry ignition tube about one-third full of lead nitrate which has been finely powdered, and *thoroughly dried.* Connect the ignition tube with a dry bottle, and finally with the water pan ; the arrangement is similar to that in **Fig. 15**, except that the flask is replaced by an ignition tube. The small bottle must be surrounded by a mixture of ice (or snow), and salt. Heat the ignition tube gently, and when the evolution of gas has once begun, care must be taken that the tube is not suffered to cool, so as to allow the water to suck back from the water pan. Red fumes will fill the delivery tubes, and will condense in the small bottle to a brownish-yellow liquid if the experiment is successful. A colorless gas will collect at the water pan ; it is oxygen, as may be shown by the insertion of a glowing splinter. The chemical action may be thus represented :—

$$\underset{\text{Lead nitrate.}}{PbN_2O_6} = \underset{\text{Lead oxide.}}{PbO} + O + \underset{\text{Nitrogen peroxide.}}{2NO_2}.$$

The experiment just performed is interesting, as showing the transformation of a substance which is usually a gas, into a liquid; in this case, it was only necessary to lower the temperature. Many other gases may be liquefied in the same manner, by being cooled to a low temperature; and by the application at the same time of a very great pressure, it has been found possible to liquefy all known gases, even oxygen, nitrogen and hydrogen, which until recently were regarded as permanent or incondensable gases.

54. **Other Oxides of Nitrogen.**—A fourth oxide of nitrogen is an unstable, white, solid compound whose symbol is N_2O_5. It is called **nitric anhydride,** and is closely related to nitric acid. Nitric acid we have already used, and have learned that its symbol is HNO_3. If the oxide N_2O_5 be treated with water the action which takes place may be represented by the equation:—

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Nitric anhydride.}}{N_2O_5} = H_2O, N_2O_5 = \underset{\text{Nitric acid.}}{2\,HNO_3},$$

which expresses the fact that, by the union of one molecule of water and one molecule of nitric anhydride, there are formed two molecules of nitric acid. On account of this reaction, nitric acid may be, and is sometimes regarded as a *compound* of nitric anhydride and water, and its formula may be written, H_2O, N_2O_5. The origin and propriety of the term **nitric anhydride** now becomes apparent; for this oxide of nitrogen, although it is obtained directly from nitric acid only with difficulty, may evidently be regarded as nitric acid deprived of water; that is, rendered **anhydrous.**

55. There is still a fifth oxide of nitrogen the symbol of which is N_2O_3. This compound may be formed as a brownish-red gas, similar to the NO_2 and mixed with some of the latter gas, by heating together strong nitric acid and common starch. The compound is called **nitrous anhydride.**

Exp. 21.—Into a flask of about 250 c. c. capacity, put 50 c. c. of strong nitric acid, and 5 grms. of starch. Warm the flask gently and as soon as the mixture begins to turn reddish-brown remove the lamp. The experiment should be performed where there is a good draft of air, as the red fumes are copiously evolved when the action once begins.

56. The oxides of nitrogen, then, are —

Nitrogen protoxide, N_2O;
Nitric oxide, NO;
Nitrous anhydride, N_2O_3 (from which we have **nitrous acid, HNO_2**);
Nitrogen peroxide, NO_2;
Nitric anhydride, N_2O_5 (from which we have **nitric acid, HNO_3**).

57. These five bodies are all **chemical compounds**; they are definite and constant in composition, and all differ essentially from their elementary constituents and from each other, as the experiments we have performed with several of them have demonstrated. It is, therefore, obvious that two of the elements are capable of combining in several proportions to form definite chemical compounds; and what is here proved of two of the elements we shall hereafter find to be true of all, although not of every couple; so that the series of oxides of nitrogen is but one illustration of a most comprehensive law. The difference between a mechanical mixture and a chemical compound does not on this account become less marked. The possible **mixtures** of nitrogen with oxygen are innumerable; the known **combinations** of these two elements are only five: two volumes of nitrogen combining chemically with either one, two, three, four or five volumes of oxygen, and with no other proportions whatsoever. As for volumes, so for weights: the proportional weight of oxygen in these oxides rises by definite leaps from the first member of the series to the last.

This definite, step-by-step mode of forming chemical compounds is one of the most characteristic, as it is one of the most general, facts of chemistry; it is the habitual mode in which the force called **chemical** ordinarily acts. The abstract results of observation and experiment may be expressed in the following proposition, often called the **Law of Multiple Proportions**: *If two bodies combine in more than one propor-*

tion, the ratios in which they combine in the second, third and subsequent compounds, are definite multiples of those in which they combine to form the first.

58. **Air a Mixture.** — The distinction between a mechanical mixture and a chemical combination may be illustrated by the differences between common air and the oxides of nitrogen. Some of the considerations which go to show that air is simply a mechanical mixture of oxygen and nitrogen are as follows: —

In the first place, while in the oxides of nitrogen the two elementary gases bear to each other some simple relation in respect to both volume and weight, in air they are mixed in the far from simple proportion of 20.96 measures of oxygen to 19.04 measures of nitrogen, or 23.18 parts by weight of oxygen to 76.82 parts of nitrogen; moreover, if 23.18 parts of oxygen are mixed with 76.82 of nitrogen, there is no development of either light, heat or electricity, such as usually attends the formation of a chemical compound; and the physical characteristics of the mixture are such as should, according to calculation, belong to a mere mixture of the gases.

Again, if nitric oxide be brought into contact with air, suffocating red fumes of nitrogen peroxide are formed; but if the nitric oxide be brought into contact with nitrogen protoxide, no fumes are produced, although this gas contains as much oxygen as common air. These experiments go to show that, while in nitrogen protoxide the oxygen is held in chemical combination, in air it is free.

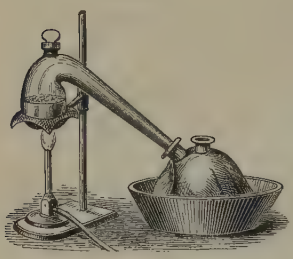
Further evidence that air is a mere mixture is afforded by its behavior towards water. All gases are soluble in water to a greater or less extent, each one dissolving in a certain fixed and definite proportion at any given temperature. If pure water be exposed to nitrogen protoxide, it will dissolve a certain amount of that gas, which may be recovered unchanged by boiling the water. When water which has been exposed to the air is boiled, a gaseous mixture containing oxygen and nitrogen is given off (**Exp. 10, § 33**); but it has been found that

the gases are mixed in a different proportion from that in which they exist in the atmosphere. The water, in fact, dissolves out from the air a quantity of oxygen, just as if no nitrogen were present; at the same time it dissolves nitrogen to precisely the same extent that it would dissolve that gas if there were no oxygen in the air.

59. **Nitric Acid** (HNO_3).—In the preparation of the various oxides of nitrogen we have used either nitric acid or a compound which we have designated as a *nitrate*, as, for example, ammonium nitrate in **Exp. 17**, and lead nitrate in **Exp. 20**. We now proceed to a study of those compounds, and, in the first place, of nitric acid itself. Two abundant sources of this material are found in nature and are familiar as articles of commerce. Saltpetre or nitre, a whitish saline crystallized substance, now mainly brought from India, is one of these sources; a similar substance, known in commerce as "nitrate of soda," is collected on a desert tract in Chili and Peru, and forms a valuable article of export from those countries. These two substances differ from each other only in this,—that the first contains **potassium**, the second the very similar element **sodium**, in either case combined with definite proportions of the elements nitrogen and oxygen. By the reaction of **sulphuric acid** (oil of vitriol) on either of these two substances, **nitric acid** is obtained.

Exp. 22.—Into a tubulated glass-stoppered retort of 250 c. c. capacity, put 40 grammes of powdered potassium nitrate, or, better, 34 grammes of powdered sodium nitrate, if it can be obtained, and through the tubulure pour 50 grammes of strong sulphuric acid, which has been weighed out in a bottle previously counterpoised upon the balance with shot or coarse sand. Imbed the bottom of the retort in sand contained in a small iron pan placed over the gas-lamp on a ring of the iron stand. Thrust the neck of the retort into a receiver with two tubulures; the retort-neck should fit the tubulure of the receiver with tolerable accuracy. The second tubulure of the receiver should be left open, or loosely covered with a bit of glass, in order to avoid the possibility of any pressure being created within the retort during the operation. Place the receiver in a pan of cold water, and cover it with cloth or bibulous paper, which must be kept

Fig. 17.



wet during the distillation. (See Fig. 17.) Heat the sand-bath *moderately* (that the frothing which occurs may not become too violent); reddish vapors appear for a moment, then disappear, and a yellowish fuming liquid begins to condense in the neck of the retort and to run down into the receiver. When all frothing has ceased and the mass in the retort is in a state of tranquil fusion, while very little liquid passes over into the receiver, the lamp is to be put out.

The very acid, corrosive and poisonous liquid in the receiver is **nitric acid**; its faint color is not its own, but is due to the presence of a compound of nitrogen and oxygen already described (NO_2). Transfer the liquid to a glass-stoppered bottle, and keep it for future use. In all manipulations with nitric acid, it is desirable to avoid getting it upon the skin, since it produces rather permanent yellow stains.

As the retort cools, the residue solidifies into a white, saline mass, which must be dissolved out of the vessel by heating it with water after the apparatus has become thoroughly cold. It will be observed that the liquid sulphuric acid which was used has disappeared, although the saline residue is still intensely acid.

60. **Nitric Acid** is much used in the arts, and is prepared on the large scale from the same materials as here employed. The retorts are huge iron cylinders or kettles and the acid is collected in stoneware bottles. The pure acid is colorless and is about half as heavy again as water. It may be mixed with water in all proportions.

Exp. 23.—To about 1 c. c. of the nitric acid obtained in the last experiment add 10 times its bulk of water. Notice the sour taste by touching a drop of this diluted acid to the tip of the tongue. Into the solution thrust a strip of *litmus paper;* it will be turned red, showing that in spite of the amount of water added, the liquid is still strongly acid. Litmus is a blue coloring matter, prepared from various lichens. Unsized paper, colored with a solution of litmus in water, is a convenient test for many acids, which, as a rule, change the color of the paper from blue to red.

61. **Acids, Bases and Salts**.—Nitric acid is an example of the class of bodies to which the term **acid** is generally applied. There is a class of bodies which act upon vegetable colors in just the opposite way from the acids, and will in fact *neutralize* their action in many cases. As an example of these substances, which are generally spoken of as **bases**, and which when soluble in water have what is called an *alkaline* reaction, we may take caustic potash.

Exp. 24.—Dissolve about one gramme of caustic potash in 20 c. c. of water. Notice the character of the solution by rubbing a little between the fingers, and by touching a small drop to the tip of the tongue. Into the liquid thrust the litmus paper, which was reddened by the nitric acid in **Exp. 23.** It will be turned blue.

The terms acid and base which we have used cannot be defined with exactness, because they are not applied by chemists with uniform precision to well-defined classes of substances. We may say, however, in general terms, that the **acids** commonly possess a sour taste and act in a peculiar way upon vegetable colors (as nitric acid reddened the litmus paper in **Exp. 23**). The acids are usually compounds of hydrogen, oxygen and some one other chemical element, as, for example, nitric acid (HNO_3); **bases**, likewise, are compounds of hydrogen, oxygen and some one other chemical element, as, for example, caustic potash (KHO); but while certain elements in uniting with hydrogen and oxygen form by preference acids, other elements form by preference bases. The so-called **non-metallic** elements, such as nitrogen, sulphur, etc., generally form **acids**: for example, nitric acid (HNO_3) and sulphuric acid (H_2SO_4). The **metallic** elements, such as potassium, sodium, copper, etc., form **bases**; thus caustic potash or potassium hydrate (KHO), sodium hydrate ($NaHO$) and copper hydrate (CuH_2O_2), are bases.

An important characteristic of the acids and bases is that they have the power, when one of either class is brought into contact with one of the other and opposite class, of forming new compounds possessing the characters of neither the acid or base from which the new compound, or **salt** as it is called has been formed.

62. The relations between **acids** and **bases** may be illustrated by the following experiment :—

Exp. 25.—To one-third of the nitric acid of Exp. 22, § 59, diluted with twice its bulk of water, add cautiously a rather dilute solution of caustic potash (potassium hydrate, **KHO**) until the mixture turns litmus-paper neither red nor blue. Evaporate the solution in a porcelain dish, taking care that the liquid does not actually boil, until a drop taken out on the end of a glass rod becomes nearly solid on cooling. Then remove the lamp, and allow the dish to become cold. The crystals which will separate from the liquid are potassium nitrate, a compound which has already been used in the manufacture of nitric acid. The change that has taken place may be thus symbolized :—

HNO_3	+	KHO	=	KNO_3	+	H_2O.
Nitric acid.		Caustic potash.		Potassium nitrate.		Water.

The water in which the nitric acid and caustic potash were dissolved, together with that set free by the reaction, has for the most part been removed by evaporation. It might have been removed entirely if the evaporation had been carried further. The potassium nitrate would then be obtained as a white crystalline substance, but not in well-defined crystals.

When, as in the above experiment, an acid and a base are brought into contact, there is formed, besides water, a new compound. This compound is called a **salt**, the name being applied to it on account of the general resemblance which this class of compounds bear to common salt, — one of the earliest known and most familiar of saline bodies.

63. If we compare the formula of nitric acid (HNO_3) with that of potassium nitrate (KNO_3), we shall observe a striking resemblance between the two ; the two formulæ are in fact identical, except that in the one case we have **K**, the symbol for potassium, where in the other we have **H**, the symbol for hydrogen. Potassium nitrate is only one of a class of analogous compounds called **nitrates**; the formula of each member of the class is that of one or more molecules of nitric acid, (HNO_3, $H_2N_2O_6$, etc.,) except that the hydrogen is replaced by some metallic

element. We have, indeed, already used several of these nitrates. Thus in **Exp. 20**, we used lead nitrate, the symbol of which is PbN_2O_6, and in **Exp. 19**, we prepared copper nitrate which remained in the solution, and the symbol of which is CuN_2O_6.

As the *nitrates* correspond to *nitric acid*, so corresponding to every acid, there is a series of salts, the name common to all the series being derived from the name of the acid. Thus corresponding to sulphuric acid there are numerous sulphates, corresponding to phosphoric acid there are phosphates, to oxalic acid oxalates, etc. As will be noticed in the cases above mentioned, the acid is designated by a term ending in *ic*, and the term applied to the salts ends in *ate;* if, however, the name given to the acid ends in *ous*, the name given to the salts ends in *ite;* thus, corresponding to nitr*ous* acid we have a series of nitr*ites;* thus, nitrous acid, HNO_2, potassium nitrite, KNO_2.

Further use of the terms Acid and Base.—The term **acid**, besides being used as defined in § 61, is applied to certain bodies which are destitute of oxygen, like chlorhydric acid (HCl). These acids are those formed by the union of hydrogen with some member of the chlorine group (see page 65), and a few others. The salts corresponding to such acids are designated by terms ending in *ide;* thus we have chlorides, bromides and fluorides from chlorhydric, bromhydric and fluorhydric acids respectively.

The term **base** is sometimes used to denote certain compounds which contain no hydrogen. If potassium oxide (K_2O), which may be formed by heating metallic potassium in dry air or oxygen gas, be treated with nitric acid, the following reaction will take place:—

$$K_2O + 2\,HNO_3 = 2\,KNO_3 + H_2O.$$

The same "salt," potassium nitrate (KNO_3), is produced as in Exp. 25, where potassium hydrate and nitric acid were brought together. On account of their taking part in such reactions as these, the anhydrous oxides of the metallic elements are often spoken of as bases. In some cases the oxide is more commonly employed than the hydrate, or base proper, in neutralizing acids and in forming salts. This is the case with oxide of lead.

Exp. 26.—Put the nitric acid which remains from **Exp. 22**, into an evaporating dish, dilute with twice its bulk of water, and add finely powdered litharge as long as it readily dissolves. Evaporate the solution carefully to dryness, using a very gentle heat. There remains a white saline substance which is lead nitrate such as was used in **Exp. 20.** Its formation is thus represented :—

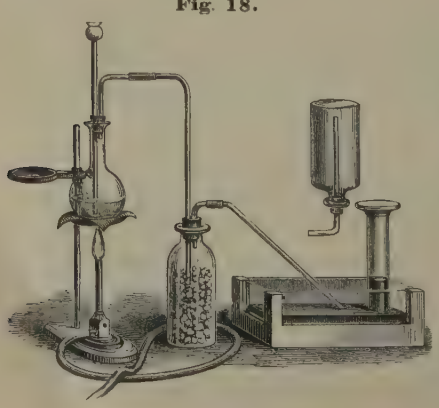
$$\underset{\text{Lead oxide.}}{PbO} + 2HNO_3 = \underset{\text{Lead nitrate.}}{PbN_2O_6} + H_2O.$$

The term **anhydride** (or more definitely, *acid anhydride*) is commonly applied to an oxide of a non-metallic element, which in combination with the elements of water forms an acid, as was illustrated by nitric anhydride in § 54. To these anhydrides the term *acid* was formerly applied, as well as to the acids proper. To distinguish between the two sorts of compounds, the terms *anhydrous* and *hydrated* were employed ; thus, N_2O_5 was known as anhydrous nitric acid, and HNO_3 as hydrated nitric acid.

NITROGEN AND HYDROGEN.

64. Nitrogen and Hydrogen.—While there are five compounds of nitrogen with oxygen, there is but one known compound of nitrogen and hydrogen. This is a gas, and may be readily prepared from ammonia-water,—the *aqua ammoniæ* of the druggists.

Fig. 18.



Fill a flask of 250 to 500 c. c. capacity about half full of the strongest ammonia-water to be had at the druggist's. Close the flask by a cork provided with a funnel-tube and an exit-tube ; carry the delivery-tube to the bottom of a tall bottle, having a capacity of at least a litre, and filled with fragments of quick-lime. When the ammonia-water in the

flask is gently boiled, the gas which passes off will be deprived of moisture by the quick-lime, and will issue dry from the bottle ; it may be collected over mercury, or by displacement, as shown in the figure (Fig. 18). The gas is so extremely soluble in water, that it cannot be collected over the ordinary water-pan ; as it has little more than half the density of atmospheric air, it can be readily collected by displacement. When thus collected, the gas should be allowed to pass into the *very loosely* corked bottle, until a piece of turmeric paper, held at the mouth, is immediately turned brown ; the delivery-tube is then withdrawn, and the mouth of the bottle is tightly closed with a caoutchouc or glass stopper.

If the gas be collected over mercury, the flask must be provided with a very long funnel-tube ; for the pressure to be overcome by the gas in forcing its way through even a few centimetres of mercury is quite considerable, and unless the funnel-tube were long enough to sustain a column of liquid exerting an equal pressure, the liquid in the flask would be forced out through this tube.

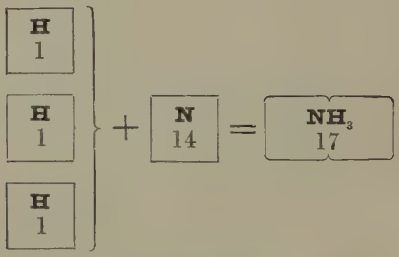
The gas thus obtained is transparent and colorless, possesses an extraordinarily pungent odor which provokes tears, and has an acrid, alkaline taste. It will be found to be uninflammable, and is, of course, irrespirable. It turns red litmus to blue most energetically. One measure of water at 0° dissolves 1,049 measures of the gas.

The ready solubility of **ammonia-gas** may be illustrated as follows : Fill a stout glass tube — an ignition-tube, for example, — over mercury with the gas ; grasp the tube by the top, and, holding it upright, dip its mouth into a vessel of water. The water will rush up the tube, if the gas be pure, with a force which might break the tube, if too thin.

65. The solution of ammonia if exposed to the air, or placed in a vacuum, or simply boiled, loses all its gas. When the gas is cooled to 0° and subjected to a pressure of $4\frac{1}{2}$ atmospheres, it is converted into a transparent mobile liquid. The gas may also be liquefied at the ordinary pressure if cooled to —40°. **Liquid ammonia** in passing into the gaseous state absorbs a large amount of heat from surrounding objects. In certain machines for the production of ice artificially, advantage is taken of this

fact, the necessary cooling of the water being produced by the rapid evaporation of liquefied ammonia-gas, in contact with the vessel containing the water.

66. Analysis of dry **ammonia-gas** has shown that it is made up of **nitrogen** and **hydrogen** in the proportion of one volume of nitrogen to three volumes of hydrogen, the four volumes of the elementary gases being condensed to two volumes in the compound. The formula of its molecule is NH_3, and its composition may be represented by the diagram, —



67. Ammonium Salts.—Since ammonia-water gives off the gas so easily when boiled or even when exposed to the air, it might seem, at first sight, that it was a case of simple physical solution; there is, however, good reason for considering that each molecule of ammonia is in combination with a molecule of water, in the form of the compound NH_3, H_2O or NH_5O. This compound may be supposed to be dissolved in the water present in excess of what is necessary to form the compound. When ammonia-water is mixed with nitric acid, a reaction occurs like that which takes place when nitric acid is mixed with a solution of caustic potash (**Exp. 25, § 62**); there is formed a salt called **ammonium nitrate,** resembling potassium nitrate; but, in order to bring out the resemblance, the elements of the compound of ammonia and water must be so arranged as to exhibit its analogy with caustic potash, whose formula is **KHO**. For that purpose, its formula must be written $(NH_4)HO$, so that the group of elements NH_4 shall stand in the formula of ammonia-water where the element potassium stands in the formula of caustic

potash. The reaction between ammonia-water and nitric acid may then be represented by the equation, —

$$\underset{\text{Ammonia-water.}}{(NH_4)HO} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Ammonium nitrate.}}{(NH_4)NO_3} + \underset{\text{Water.}}{H_2O},$$

just like —

$$KHO + HNO_3 = KNO_3 + H_2O.$$

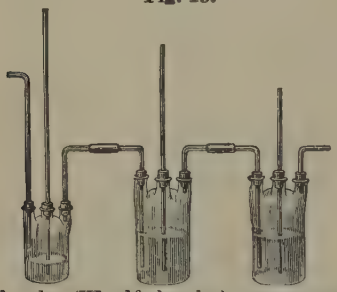
If now the formula of ammonium nitrate, $(NH_4)NO_3$, be compared with that of nitric acid, HNO_3, it will appear that the group of atoms NH_4 replaces the atom **H**, just as the atom **K** did in the formula of potassium nitrate: for this reason it has been found convenient to give to this group of atoms a name bearing some resemblance to the names of metals; and it has, therefore, been called **ammonium**. Ammonium is known only in its compounds; many attempts have been made to obtain it in a free state, but hitherto in vain: as soon as the group of atoms escapes from combination, it is resolved into ammonia and hydrogen. The important compounds into which ammonium enters, commonly called the **salts of ammonium**, will be studied hereafter in immediate connection with the analogous salts of sodium and potassium.

68. **Ammonia** exists in very minute quantity in the atmosphere, and hence in rain-water, fog and dew. It is given off by putrefying animal and vegetable substances containing nitrogen, and almost every process of slow oxidation in the presence of air and moisture is attended with the formation of ammonia or ammonium salts. The chief source, however, of ammonium compounds is the decomposition, either by putrefaction or by destructive distillation, of nitrogenous organic matter. The distillation of bones and animal refuse, for the purpose of making bone-black, yields a large amount of ammoniacal liquor, which was formerly the principal source of ammonium compounds. The horns of deer used to be thus distilled; whence the name "hartshorn." At present, the destructive distillation of coal in gas-works furnishes the great bulk of ammonium compounds used in the arts.

69. The solution of ammonia-gas in water is a reagent continually required, as a test, in the laboratory, and much used in the arts. The solution is colorless, intensely alkaline, has a caustic taste, and, when concentrated, blisters the skin; it is lighter than water, and so much the lighter in proportion to the amount of ammonia that it contains. The solution may be prepared from a mixture of **ammonium chloride** and **slaked lime.**

Exp. 27. — Mix 25 grms. of ammonium chloride, a substance generally sold under the name of *sal ammoniac*, with about the same weight of cold, freshly-slaked lime. Introduce the mixture into a flask of 500 c. c. capacity, and place the flask on a sand-bath over the gas-lamp. Close the mouth of the flask with a good cork, provided with a delivery-tube so bent as to connect conveniently, by means of a caoutchouc connector, with the first of the series of three-necked bottles (Woulfe-bottles) represented in Fig. 19. On heating the mixture, ammonia-gas will be disengaged, and will be absorbed by the water in the Woulfe-bottles.

Fig. 19.



The first of this series of bottles is smaller than the rest, and is not filled so full of water as the others; it should be kept cool by immersion in cold water; the delivery-tube coming from the flask into this bottle must *not* dip into the water at all, so that it will be impossible for any water to suck back into the flask, should the gas suddenly cease to come off from the dry mixture. The construction of the apparatus will be easily understood from the figure; the open tube which dips beneath the water in each bottle is a safety-tube, which by admitting air into any bottle in which a partial vacuum may happen to be created by rapid absorption, prevents the contents of the succeeding bottle from flowing back into it. In order to show the action of the safety-tubes, the open tube in the first bottle may be closed for a moment with the finger, and the bottle shaken very gently. Water will be immediately forced back from the second bottle through the connecting-tube to fill the vacuum caused by the absorption of the

ammonia-gas ; but the moment the finger is removed from the safety-tube, air will enter through the latter to fill the vacuum, and the water in the connecting-tube will fall back into the second bottle. The ammonia-gas can not avoid three separate contacts with water as it passes through the apparatus, so that all the gas is sure to be absorbed ; the contents of the first bottle will not be as pure as those of the succeeding. In this experiment the gas will be mostly absorbed in the first and second Woulfe-bottles.

The reaction between the ammonium chloride and the slaked lime is represented by the following equation : —

$$\underset{\text{Ammonium chloride.}}{2\,NH_4Cl} + \underset{\text{Slaked lime.}}{CaH_2O_2} = \underset{\text{Ammonia.}}{2\,NH_3} + \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Water.}}{2\,H_2O.}$$

Ammonium chloride is a compound which may be obtained by bringing together dry ammonia, NH_3, and dry muriatic-acid gas, HCl.

$$NH_3 + HCl = NH_4Cl.$$

It may obviously be regarded as a compound of the group called **ammonium,** NH_4, with the element **chlorine** ; from this view is derived the name **ammonium chloride.** Slaked lime is prepared by adding water to quick-lime, which is chemically the oxide of the metal **calcium.**

$$CaO + H_2O = CaH_2O_2.$$

CHAPTER VII.

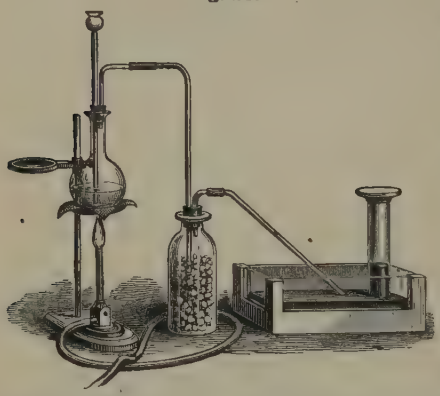
CHLORHYDRIC ACID.

70. **Muriatic** (sea-salt) acid, called in modern nomenclature **chlorhydric acid,** is a liquid which has been known for centuries, and is to-day an article of commerce, largely employed in the useful arts. The pure acid is a **gas,** as ammonia is ; the liquid muriatic acid of commerce is only an aqueous solution of

this gas, and gives it up when heated, precisely as ammonia-water yields ammonia-gas.

This operation may be conveniently performed in the apparatus shown in Fig. 20. About 250 c. c. of the commercial acid is poured into the flask, which is then moderately heated: the gas disengaged is charged with aqueous vapor, which needs to be removed before the gas is collected. For this purpose the delivery-tube is carried to the bottom of a bottle filled with pieces of pumice-stone saturated with strong sulphuric acid: the moisture of the gas is greedily absorbed by the large surface of acid with which the gas comes into contact, as it is forced upward through the acid-soaked stone. The dry, colorless, transparent gas must be collected over mercury, for it is extremely soluble in water.

Fig. 20.

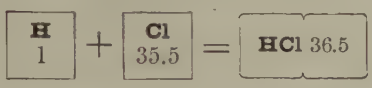


The gas is strongly **acid** in taste and reaction on vegetable colors, provokes violent coughing and is wholly irrespirable. It is neither combustible, nor will it support combustion. The gas is somewhat heavier than air: it is very soluble in water, and may be condensed to a liquid, although with difficulty.

The avidity of water for chlorhydric acid gas may be neatly shown by thrusting a bit of ice into a small cylinder of the dry gas standing over mercury: the ice instantly melts, and the gas as quickly disappears.

71. The composition of the gas has been determined, both by analysis and by synthesis; and it has been found that one volume of **hydrogen** is combined with one volume of the elementary gas **chlorine** (**Cl**) to form two volumes of **chlorhydric acid.** The molecule of chlorhydric acid will be represented by the formula **HCl**; and, as the specific gravity of chlorine, that

is, the weight of any volume compared with an equal volume of hydrogen, is 35.5, the following diagram represents the composition of this important compound, both by volume and by weight : —



72. The **muriatic acid** of commerce is made from the most abundant and cheapest of all the natural compounds of chlorine, — common salt, whose chemical name is **sodium chloride,** and whose formula is **NaCl**. This substance supplies the chlorine : the necessary hydrogen is obtained from common **sulphuric acid** (oil of vitriol), whose composition, as expressed in its formula H_2SO_4, we have already become familiar with. The reaction is somewhat various, according to the proportion of sulphuric acid employed ; it may be either of the reactions expressed in the following equations : —

NaCl	+	H_2SO_4	=	**HCl**	+	**$HNaSO_4$**;
Sodium chloride.		Sulphuric acid.		Chlorhydric acid.		Hydrogen Sodium sulphate.
2 NaCl	+	H_2SO_4	=	**2 HCl**	+	**Na_2SO_4.**
						Sodium sulphate.

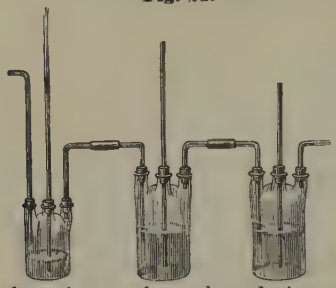
In the first of these reactions, only one-half of the hydrogen in each molecule of sulphuric acid is replaced by sodium ; in the second, both atoms of hydrogen are thus replaced. The first reaction requires more sulphuric acid, in proportion to the amount of the product than the second, but is accomplished with less wear of the apparatus, because a more moderate heat suffices for the first than for the second reaction.

On the manufacturing scale, the salt and sulphuric acid are heated in large iron cylinders, and the evolved gas is absorbed by water contained in a series of stoneware Woulfe-bottles. The ordinary commercial acid contains from 30 to 40 per cent by weight of real acid.

Exp. 28. — Place 30 grms. of dry (or better, fused) coarsely powdered

salt, in a flask of a litre capacity, provided with a delivery-tube which can be conveniently connected by a caoutchouc connector with a series of small Woulfe-bottles, such as is represented in Fig. 21. Pour 50 grms. of strong sulphuric acid upon the salt, and immediately cork the flask, place it upon a sand-bath on the iron-stand and connect the delivery-tube with the Woulfe-bottles. The tubes by which the gas enters the bottles should barely dip beneath the water contained in them, inasmuch as the solution of chlorhydric acid is heavier than water : the bottles should not be more than half full, for the water becomes hot, and increases considerably in bulk. As hot water holds less gas in solution than cold water, it is not amiss to place each three-necked bottle in a vessel of cold water. The first Woulfe-bottle should contain but a small quantity of water, and the tube coming from the flask should not dip into this water. The contents of the flask must be *very gradually* and moderately heated, else a violent frothing is liable to occur, which would spoil the experiment. The acid will be purer in the second bottle than in the first, in the third than in the second, and so forth.

Fig. 21.



73. The uses of **chlorhydric acid** are very numerous : it is employed in making chlorine, potassium chlorate, and "chloride of lime" (bleaching powder); in preparing ammonium chloride and tin chloride ; in the manufacture of gelatin ; for dissolving metals, either by itself or mixed with nitric acid ; and it is one of the most useful reagents in the chemical laboratory.

74. **Chlorhydric acid**, as has already been stated (§ 63), differs from the other acids with which we have become acquainted in that it contains no oxygen.

As there are certain compounds called **nitrates** whose formulæ may be derived from that of **nitric acid** by replacing the symbol of hydrogen in the acid by that of some metallic element ; so there is a series of compounds, the formulæ of which may be derived from that of **chlorhydric acid** by putting the symbol of a metallic element in the place of the symbol of hydrogen in the acid. These compounds

are called **chlorides**: thus sodium chloride, common salt, is **NaCl**. Chlorides are formed in some cases by treating the metal with chlorhydric acid, as in the formation of zinc chloride ($ZnCl_2$), Exp. 11, § 35: in other cases they are formed by treating the oxide, or the hydrate, of the metal with chlorhydric acid, as may be seen in these equations: —

NaHO	+	**HCl**	=	**NaCl**	+	H_2O;
Sodium hydrate.				Sodium chloride.		
Ag_2O	+	**2 HCl**	=	**2 AgCl**	+	H_2O;
Silver oxide.				Silver chloride.		
CuO	+	**2 HCl**	=	$CuCl_2$	+	H_2O.
Copper oxide.				Copper chloride.		

If the formula of silver chloride (**AgCl**) be compared with that of zinc chloride ($ZnCl_2$), this difference will be observed between them, — that while the molecule of silver chloride may be regarded as a molecule of chlorhydric acid (**HCl**), in which the atom of hydrogen (**H**) is replaced by an atom of silver (**Ag**), the molecule of zinc chloride must be regarded as formed from two molecules of chlorhydric acid (H_2Cl_2) by replacing two atoms of hydrogen (H_2) by one atom of zinc (**Zn**). Now, there is a class of metals which, like silver, replace hydrogen atom for atom: these metals are said to be **univalent**. There is another class of metals which act like zinc in replacing hydrogen: they are said to be **bi-valent**. The same distinction is seen in the other compounds of these elements: thus, sulphuric acid being H_2SO_4, zinc sulphate is $ZnSO_4$, and silver sulphate is Ag_2SO_4; nitric acid being HNO_3, zinc nitrate is ZnN_2O_6, and silver nitrate is $AgNO_3$. It will appear hereafter that there are elements which are tri-valent, quadri-valent, etc. In general terms, the **replacing-power** of any element with respect to hydrogen is called its **quantivalence**; this quantivalence of an element may be learned, not only from the number of hydrogen atoms which the atom of the element can replace, but also from the number of hydrogen atoms with which it can combine: thus, from the formula of chlorhydric acid, **HCl**, we learn that chlorine is here uni-valent, as the atom of chlorine combines with only a single atom of hydrogen. [See also page 288.]

75. **Aqua Regia (Royal Water).**—This name was given by the alchemists to a mixture of chlorhydric and nitric acids, because of its power to dissolve **gold**, the "king of metals."

Exp. 29. — Place a few square centimetres of genuine gold-leaf at the bottom of a test-tube, and pour upon the gold a little strong chlorhydric acid ; put some gold-leaf in a second test-tube, and pour upon it a few drops of nitric acid : neither acid attacks the gold, which remains undissolved. If the contents of the two test-tubes be mixed together in either tube, the gold-leaf will almost immediately dissolve.

The efficacy of **aqua regia** as a solvent of gold depends upon the fact that the nitric and chlorhydric acids mutually decompose each other. Chlorine is set free, and, as it issues from its combination with hydrogen, acts on the gold much more energetically than it would in its ordinary condition. The chlorine in this case is said to be in the **nascent** state.

There are numerous cases in which bodies, which do not unite under ordinary conditions, are capable of chemical combination at the instant when they are disengaged from other compounds ; and the phrase, "*in the nascent state*," just used, is one of some convenience, although it must not be supposed to explain, or in any way to account for, the phenomena with reference to which it is employed.

76. The practical importance of a knowledge of the atomic weights in calculating the proportional amounts of the different substances taking part in any case in a chemical action, has already been explained in § **36**, and may, at this point, be further illustrated as follows. In the manufacture of chlorhydric acid, for instance, suppose it were required to ascertain how much sulphuric acid would be necessary to decompose 100 kilos. of salt, bearing in mind that the result may be effected according to either of the two actions formulated on page 51.

The molecular wt. of	**NaCl**	is $23 + 35.5$	$=$	58.5
" " "	$\mathbf{H_2SO_4}$	is $2 + 32 + 4 \times 16$	$=$	98
" " "	$\mathbf{HNaSO_4}$	is $1 + 23 + 32 + 64$	$=$	120
" " "	$\mathbf{Na_2SO_4}$	is $46 + 32 + 64$	$=$	142
" " "	**HCl**	is $1 + 35.5$	$=$	36.5

The weight of the sulphuric acid needed in the two cases is ascertained by solving the following proportions : —

First reaction	58.5	:	98	=	100	:	x (= 167.52)
	Mol. wt. **NaCl**		*Mol. wt.* H_2SO_4		*No. kilos.* **NaCl** used.		*No. kilos.* H_2SO_4 needed.
Second reaction	117	:	98	=	100	:	x (= 83.76)
	Mol. wt. of **2NaCl**						

The weight of chlorhydric acid gas produced in the two cases will be precisely the same: it is deduced from the proportions, —

First reaction	58.5	:	36.5	=	100	:	x (= 62.39)
	Mol. wt. **NaCl**		*Mol. wt.* **HCl**		*Kilos.* **NaCl** used.		*Kilos.* **HCl** produced.
Second reaction	117	:	73	=	100	:	x (= 62.39)
	Mol. wt. **2NaCl**		*Mol. wt.* **2HCl**				

The weights of the residual sodium salts in the two cases may be deduced as follows: —

First reaction	58.5	:	120	=	100	:	x (= 205.13)
	Mol. wt. **NaCl**		*Mol. wt.* **HNaSO$_4$**		*Kilos.* **NaCl** used.		*Kilos. of* **HNaSO$_4$**
Second reaction	117	:	142	=	100	:	x (= 121.37)
	Mol. wt. **2NaCl**		*Mol. wt.* **Na_2SO_4**				*Kilos. of* **Na_2SO_4** produced.

CHAPTER VIII.

CHLORINE, BROMINE, IODINE AND FLUORINE.

CHLORINE (Cl).

77. **Chlorine** is an abundant element and very widely distributed in nature. It exists chiefly in combination with sodium as **sodium chloride,** which is called rock-salt or sea-salt, accordingly as it is found in beds in the earth, or dissolved in the water of the ocean. Every litre of sea-water will yield about

5 litres of chlorine gas. Besides sodium chloride, sea-water contains small quantities of the chlorides of several other metals; there are numerous minerals, also, which contain chlorine.

78. **Chlorine** can readily be prepared from **chlorhydric acid** by removing the hydrogen of that acid by chemical means.

Exp. 30. — In a flask of about 500 c.c. capacity, furnished with a suitable delivery-tube, place 8 or 10 grms. of coarsely-powdered manganese binoxide; pour upon it 20 or 30 grms. of common muriatic acid, and gently heat the mixture. Chlorine will soon be disengaged, and may be recognized by its peculiar color. Being very heavy, the gas may best be collected by displacement in dry bottles placed in the open air or in a case or box provided with an efficient draft. It may also be collected over warm water or brine in the water-pan. It can not be well collected over water at the ordinary temperature, since it is rather easily soluble therein; though the difficulty may be obviated in part by evolving the gas rapidly, or by passing the delivery-tube to the top of the bottle in which the gas is collected. It must not be left standing over water, since it would soon be entirely absorbed. In experimenting with chlorine, care must always be taken not to inhale it.

The reaction which occurs in this experiment may be thus formulated: —

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + 2Cl.$$

Manganese binoxide is a substance rich in oxygen, which, under certain conditions, it readily yields up to other elements. In the case before us, the oxygen of the manganese binoxide unites with the hydrogen of the chlorhydric acid to form water. The chlorine of the chlorhydric acid unites in part with the manganese, to form manganese chloride, and is in part left free.

79. At the ordinary temperature, **chlorine** is a gas of yellowish-green color, 2.5 times heavier than atmospheric air. Its specific gravity and atomic weight are 35.5. It is excessively irritating and suffocating, even when inhaled in exceedingly small quantities. Any attempt to breathe the undiluted gas would undoubtedly be fatal.

80. **Chlorine** is a powerful chemical agent. It combines with **hydrogen** with explosive violence when a mixture of the two gases is heated, or even exposed to sunlight.

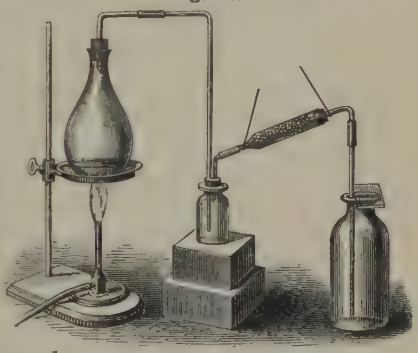
Exp. 31. — In a soda-water bottle, which must be screened from strong light by wrapping it in a towel, unless direct and reflected sunlight be excluded from the room, mix equal volumes of chlorine and hydrogen, then remove the cork and hold the mouth of the bottle in the flame of a lamp. A sharp explosion will ensue.

A mixture of the two gases may be kept in the dark for any length of time without change: in diffused daylight, they usually unite only slowly and gradually; but, in direct sunlight, the union is so instantaneous as to be attended with explosion.

81. **Chlorine** combines also very readily with many of the metals, the combination being in several instances attended with evolution of light.

Exp. 32. — Fill a bottle of at least half a litre capacity with dry chlorine gas, by displacement. Gradually sift a gramme or two of very finely-powdered metallic antimony into the bottle. The metal will instantly take fire, and fall in a glowing state to the bottom of the bottle. This fire attends the formation of a compound of chlorine and antimony, a portion of which will be seen pervading the bottle as a white smoke.

Fig. 22.



It is necessary for the success of this experiment, that the gas be thoroughly dried; this is effected by heating the flask containing the manganese binoxide and chlorhydric acid *gently*, and passing the chlorine through a tube filled with chloride of calcium. (Appendix, § 16.) It is not amiss to interpose a small bottle between the flask and the drying-tube: this bottle may be kept cool by immersion in water, and will retain a considerable portion of the moisture carried forward by the gas.

This experiment, and, indeed, all experiments with chlorine, should be performed only in places where there is a current of air sufficiently

powerful to carry away from the operator the volatile products of the reaction, together with any chlorine which may escape from the bottle.

As in the case of the union of sulphur with copper (**Exp. 1, § 2**), so here it will be seen that **burning,** as commonly understood, is in no wise peculiar to the union of oxygen with the other elements. In the act of chemical combination, heat is always evolved, and, of course, light as well, if particles of solid matter be present, and become hot enough to be luminous.

Since oxygen is very abundant, we are more accustomed to witness exhibitions of its chemical action than of that of any other element; but we must not, therefore, lose sight of the fact that among the elements, there are several which possess chemical power as great when brought into play, though not as frequently exhibited as that of oxygen.

82. A burning jet of **hydrogen,** on being introduced into a jar of **chlorine,** will continue to burn with a peculiar green light, the two gases uniting to form **chlorhydric acid;** and, by reversing the experiment, chlorine may just as well be burned in an atmosphere of hydrogen. Although chlorine is thus both combustible and a supporter of combustion, as far as **hydrogen** is concerned, it does not unite directly with either **oxygen** or **carbon.**

If a bit of paper, attached to a wire, be dipped in hot oil of turpentine, and then quickly plunged into a bottle of chlorine, it will usually take fire spontaneously, and burn with evolution of dense black fumes. On account of the volatility and ready inflammability of oil of turpentine, it is best heated upon a water-bath (Appendix, § 17), in a porcelain dish.

Fig. 23.

Exp. 33. — Thrust a burning taper, or a bit of flaming wood or paper, into a bottle of chlorine gas; the flame will become murky, and, after struggling for a moment, will go out. Much smoke is at the same time given off.

The wax, wood, paper and turpentine of the foregoing experiments, and, indeed, most of the substances ordinarily used as combustibles, contain hydrogen and carbon.

The hydrogen of these substances will burn in chlorine, that is, will unite chemically with the chlorine to form chlorhydric acid ; but the carbon will not thus unite with chlorine. Hence it is that in the experiments in question the combustion is at the expense of the hydrogen ; the hydrogen of the candle, turpentine and so forth, alone unites with chlorine ; while the carbon is set free as lamp-black or smoke.

83. **Chlorine** is a powerful **bleaching agent,** and, on this account, is of great importance in the arts. The chlorine to be used for this purpose must be moist : perfectly dry chlorine will not bleach.

This may be illustrated by passing perfectly dry chlorine through a glass tube filled with bits of colored calico. The coloring matters will not be destroyed so long as they remain dry ; but if, after the dry chlorine has been allowed to act for a few minutes, a little water be poured into the tube, so that its contents may be moistened, they will be bleached at once.

Those coloring matters which are of vegetable or animal origin are, for the most part, complex compounds of carbon, hydrogen, nitrogen and oxygen. When moist chlorine is brought into contact with them, a somewhat complicated reaction occurs : a portion of their hydrogen is, no doubt, taken out by the chlorine ; but, at the same time, some of the water which is present is decomposed, and its oxygen assists the disorganization of the compound which is to be destroyed. As a rule, the coloring matters are far more easily oxidized than the cotton cloth ; hence they can readily be removed by the action of chlorine without injury to the cloth. But, if the action of the chlorine were to be continued after the coloring matter had been destroyed, the cloth itself would gradually be burned up.

The bleaching properties of chlorine may be conveniently illustrated by means of an aqueous solution of chlorine, **chlorine-water,** which may be prepared by connecting the flask in which the gas is generated with a series of Woulfe-bottles, as in the preparation of chlorhydric acid. (Fig. 21, § 72.)

Exp. 34. — Pour into a small bottle a quantity of chlorine-water, drop into it a small quantity of a solution of indigo, and stir the mixture with a glass rod. The blue color of the indigo will be immediately destroyed.

In the same way, the color of litmus, cochineal, aniline-purple, or

of flowers, calico, and the like, can be readily destroyed by immersion in chlorine-water.

84. **Chlorine** is also employed as a **disinfectant.** It destroys noxious effluvia, either by acting on them as on coloring matters, or by simply taking away hydrogen, as in the case of **sulphuretted hydrogen**, hereafter to be studied.

85. **Oxides and Acids of Chlorine.** — Five compounds of oxygen and chlorine are recognized by chemists, although they have not all been isolated. Four of them combine with the elements of water to form acids. Of these compounds the most important is **chloric acid** ($HClO_3$) corresponding to **nitric acid** (HNO_3), and giving rise to compounds called **chlorates.** Potassium chlorate ($KClO_3$), one of these compounds, was used in **Exp. 4, § 12,** as a source of oxygen. Under the influence of heat, it is decomposed into oxygen and potassium chloride : $KClO_3 = KCl + O_3$.

One of the salts of **hypochlorous acid** (HClO), namely, **calcium hypochlorite,** is of great importance in the arts, being an ingredient of "chloride of lime," or **bleaching-powder.** This substance is used in very large quantities for bleaching purposes : its value depends upon the readiness with which it gives off chlorine under the influence of chemical agents. When it is treated with any acid, chlorine is disengaged.

Exp. 35. — At the bottom of a large, tall beaker, or other wide-mouthed glass vessel, of the capacity of two or three litres, place a small bottle containing 15 or 20 grms. of bleaching-powder. Cover the beaker with a glass plate, or sheet of pasteboard, provided with a small hole at the centre : through this hole in the cover pass a thistle-tube down into the bottle of bleaching-powder, and pour upon it several small successive portions of sulphuric acid diluted with an equal volume of water. Chlorine gas will immediately be set free from the bleaching-powder, and, falling over into the bottom of the large beaker, will gradually press out and displace the air therein contained, so that, after a short time, the beaker will be seen to be completely filled with the green gas. This is by far the easiest and most expeditious method of preparing chlorine. The heavy gas may

be ladled out of the jar with a dipper made of any small bottle, and poured upon a solution of indigo to show its bleaching power.

Exp. 36. — Soak a bit of printed calico in a half-litre of water, into which 10 or 15 grms. of bleaching-powder have been stirred. Observe that the color of the calico slowly undergoes change; then transfer the cloth to another bottle filled with very dilute chlorhydric or sulphuric acid, and take note of the rapidity with which the color is discharged. If need be, again immerse the calico in the bleaching bath, and afterwards in the dilute acid. Finally, wash the whitened cloth thoroughly in water.

BROMINE (Br).

86. **Bromine** is an element closely allied to **chlorine.** It is not found in the free state in nature but always in combination with some metallic element. **Bromides** occur in small quantities in sea-water and in the water of many saline springs. One litre of sea-water will yield from 0.0143 to 0.1005 grm. of free bromine. **Magnesium bromide** is a constituent of the uncrystallizable residue, called bittern, which remains after the sodium chloride has been crystallized out from the natural brines: at several saline springs this bittern contains so large a proportion of the bromide, that bromine can be profitably extracted from it. Most of the bromine of commerce is thus obtained.

87. At the ordinary temperature, **bromine** is a liquid of dark brown-red color, about three times as heavy as water, and highly poisonous. Its odor is irritating and disagreeable, whence the name **bromine,** derived from a Greek word signifying a stench. It boils at about 60°, but is very volatile even at the ordinary temperature of the air.

Exp. 37. — By means of a small pipette, throw into a flask or bottle of 1 or 2 litres' capacity 3 or 4 drops of bromine. Cover the bottle loosely, and leave it standing. In a short time it will be filled with a red vapor, which is bromine gas. This vapor is very heavy, more than 5 times as heavy as air and 80 times heavier than hydrogen.

88. In its chemical behavior, as well as in many of its physical properties, bromine closely resembles chlorine.

Its affinity for hydrogen, though weaker than that of chlorine, is still powerful. Like chlorine, it is an energetic bleaching and disinfecting agent. If finely-powdered metallic antimony be thrown into bromine, violent chemical action takes place. The metal burns as in chlorine, antimony bromide being formed.

89. **Bromhydric Acid** (HBr). — Like chlorine, bromine forms with hydrogen a compound in which equal volumes of the two elements (the bromine being in the state of vapor) are united without condensation. **Bromhydric acid** is a colorless, irritating gas, readily soluble in water.

Bromic acid ($HBrO_3$) is analogous to **chloric acid** ($HClO_3$). The **bromates** resemble the corresponding **chlorates.**

IODINE (I).

90. In its chemical properties **iodine** bears a striking resemblance to **bromine,** and to **chlorine**. Compounds of the element exist in sea-water and in many saline and mineral springs. The proportion of iodine in sea-water is exceedingly small, being even smaller than that of bromine ; but iodine is obtained more readily than bromine ; for iodine is absorbed from sea-water by various marine plants, which, during their growth, collect and concentrate the minute quantities of iodine which the sea-water contains, to such an extent that it can be extracted from them with profit.

91. At the ordinary temperature, **iodine** is a soft, heavy, crystalline solid of bluish-black color and metallic lustre. Its specific gravity is 4.95. It evaporates rather freely at the ordinary temperature of the air, and the more rapidly when it is in a moist condition. Its odor is peculiar, somewhat resembling that of chlorine, but weaker, and easily distinguished from it. It is but slightly soluble in water, but dissolves readily in alcohol. The atomic weight of iodine is 127.

The vapor of iodine is of a magnificent purple color, whence the name **iodine,** derived from a Greek word signifying violet-colored. This vapor is very heavy, — indeed, the heaviest of

all known gases : it is nearly 9 times as heavy as air : its specific gravity referred to hydrogen is 127.

Exp. 38. — Hold a dry test-tube in the gas-lamp by means of the wooden nippers, and warm it along its entire length, in so far as this is practicable. Drop into the hot tube a small fragment of iodine and observe the vapor as it rises in the tube. If only a small portion of the tube were heated, the vapor would be deposited as solid iodine upon the cold part of its walls.

92. Solid **iodine** is never met with in the amorphous, shapeless state in which glass, resin, coal and many other substances occur. No matter how obtained, its particles always exhibit a definite **crystalline** structure. If the iodine be melted, and then allowed to cool, or if it be converted into vapor and this vapor be subsequently condensed, crystals will be formed in either case.

93. A singular property of **iodine** is its power of forming a blue compound with **starch**.

Exp. 39. — Prepare a quantity of thin starch paste by boiling 30 c. c. of water in a porcelain dish, and stirring into it 0.5 grm. of starch which has previously been reduced to the consistency of cream by rubbing it in a mortar with a few drops of water.

Pour 3 or 4 drops of the paste into 10 c. c. of water in a test-tube, and shake the mixture so that the paste may be equably diffused through the water, then add a drop of an aqueous solution of iodine, and observe the beautiful blue color which the solution assumes. If the solution be heated, the blue coloration will disappear, but it reappears when the liquid is allowed to cool.

Dip a strip of white paper in the starch-paste and suspend it, while still moist, in a large bottle, into the bottom of which two or three crystals of iodine have been thrown. As the vapor of iodine slowly diffuses through the air of the bottle, it will at last come in contact with the starch, and after some minutes the paper will be colored blue.

This reaction furnishes a very delicate test for **iodine**. By its means it has been proved that iodine, though nowhere very abundant, is very widely distributed in nature. This reaction is also made the basis of a test for **chlorine**. Strips of paper are

smeared with starch-paste into which potassium iodide in solution has been stirred. The paper is dried and kept in stoppered bottles. When a strip of this paper is moistened and exposed to chlorine gas, the chlorine attacks the potassium iodide, potassium chloride is formed, and iodine is set free. The iodine thus set free manifests itself by imparting the characteristic blue color to the starch:—$KI + Cl = KCl + I$.

94. As has been already stated, iodine, in its chemical behavior, resembles chlorine and bromine, only its affinities are more feeble. It enters into combination with less energy than either of these elements, and is displaced by them from most of its combinations. Like them, it unites directly with the metals and with several other elements. It gradually corrodes organic tissues, and destroys coloring-matters, though but slowly. Iodine and certain of its compounds are much used in medicine and in photography.

95. **Iodohydric acid** (**HI**) is a colorless acid gas of suffocating odor, very soluble in water. It is made up of equal volumes of hydrogen and iodine vapor. The proportions by weight are 1 part of hydrogen to 127 parts of iodine. The chemical effect of the small proportion of hydrogen contained in iodohydric acid is most remarkable. Only $\frac{1}{128}$, or less than 1 per cent of iodohydric acid is hydrogen; yet this very small proportional quantity of hydrogen is competent to impart to the new compound properties possessed by neither the iodine nor the hydrogen: the acid bears no resemblance to either of its constituents.

Iodic acid (HIO_3) is analogous to **chloric** and **bromic acids.** The **iodates** correspond in composition and general character to the **bromates** and **chlorates.**

96. **Nitrogen Iodide.** — Nitrogen forms, with chlorine, bromine and iodine, a class of compounds which are very explosive. **Nitrogen chloride** is extremely dangerous, often exploding spontaneously without apparent cause. **Nitrogen iodide** is much less explosive and may safely be prepared in very small quantities.

Exp. 40. — Place 0.25 grm. of finely-powdered iodine in a porcelain capsule, pour upon it enough concentrated ammonia-water to somewhat more than cover the iodine and allow the mixture to stand during 15 or 20 minutes. Collect in several small filters (Appendix, § 15) the insoluble dark brown powder which will be found at the bottom of the liquid. Wash well with cold water and then remove the filters, together with their contents, from the funnels ; pin them upon bits of board, and allow them to dry spontaneously. The powder is the nitrogen iodide. As soon as it has become thoroughly dry, it will explode upon being rubbed, even with a feather, or jarred, as by the shutting of a door, or by a blow upon the wall or table.

97. **The Chlorine Group.** — **Chlorine, bromine** and **iodine** constitute one of the most remarkable and best-defined natural groups of elements. Whether we regard the uncombined elements or their compounds, it is impossible not to be struck with the close analogies which subsist between them.

With **hydrogen,** all of these elements unite in the proportion of one volume to one volume, without condensation, to form **acid compounds** extremely soluble in water and possessing throughout analogous properties. Moreover, each of them forms a powerful **acid** containing three atoms of **oxygen,** besides divers other compounds of obvious likeness. With **nitrogen** they all form explosive compounds. Many similar analogies will be made manifest as we proceed to study the other elements and their compounds with this chlorine group.

There is a family resemblance between these three elements as regards their **physical** as well as their **chemical** characteristics ; but with all their properties, a distinct progression is observable from chlorine through bromine to iodine. At the ordinary temperature, chlorine is a gas, bromine a liquid and iodine a solid, though, at temperatures not widely apart, they are all known in the gaseous and liquid states. The specific gravity of bromine vapor is greater than that of chlorine, and that of iodine greater than that of bromine. Chlorine gas is yellow, the vapor of bromine is reddish-brown, that of iodine violet. So with all their other properties, — chlorine will

be at one end of the scale, iodine at the other, while bromine invariably occupies the intermediate position.

The properties of the members of this group illustrate what seems to be a general principle; namely, that among the members of a natural chemical group, **chemical energy** varies in the inverse direction of the **atomic weights.** Thus, the atomic weight of chlorine is 35.5, that of bromine 80 and that of iodine 127; while the chemical energy of these elements follows the opposite order.

FLUORINE (F).

98. There is another substance, called **fluorine,** which is closely analogous to **chlorine.** It occurs tolerably abundantly in nature as **calcium fluoride** (CaF_2), in the mineral known as **fluor-spar.** Small quantities of fluorine are found also in several other minerals, in vegetable and animal substances, particularly in bones, and traces of it occur in sea-water and in various rocks and soils. Of late years a considerable mine of a fluorine mineral called **cryolite** (fluoride of sodium and aluminum) has been worked in Greenland.

99. **Fluorine** can not be readily obtained in the free state and scarcely any thing is known of it in that condition. Of all the elements, it appears to have the strongest tendency to enter into chemical combination. It is not only difficult to expel fluorine from the minerals in which it is found in nature; but, on being set free from one compound, it immediately attacks whatever substance is nearest at hand, and so enters into a new combination. Hence it is wellnigh impossible to collect it. Little or no doubt, however, is entertained as to the general nature of fluorine, since its compounds are closely analogous in many respects to the corresponding compounds of chlorine, bromine and iodine. It is to be remarked that fluorine is the only element known which forms no compound with oxygen. The symbol of fluorine is **F.** Its atomic weight is 19.

100. **Fluorhydric Acid (HF).**—With hydrogen, fluorine forms a powerful acid corresponding to chlorhydric acid and the

other hydrides of the chlorine group. It is a more energetic acid than either of these, but is specially characterized by its corrosive action upon glass. It may be readily prepared by distilling powdered fluor-spar with strong sulphuric acid; the reaction being analogous to that which occurs when common salt is treated with sulphuric acid: —

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

Since the acid rapidly corrodes glass, the process must be conducted in metallic vessels. Ordinarily, retorts of lead or platinum are employed, and the distillate is collected in receivers made of the same metals, and carefully cooled by means of ice.

The acid thus prepared always contains a small amount of water which it is difficult to remove completely. The *perfectly dry* acid, which may be made by the distillation of dry hydrogen potassium fluoride is, like that prepared as above, a very volatile, fuming liquid; it does not, however, act upon glass.

This corrosive power, possessed by moist fluorhydric acid gas, as well as by its aqueous solution, is made use of for etching glass. The graduations on the glass stems of thermometers and eudiometers may thus be made with great precision and facility: the acid is largely employed also in ornamenting glass with etched patterns.

Exp. 41. — Warm a slip of glass, and rub it with beeswax so that it shall be everywhere covered with a thin, uniform layer of the wax. With a needle, or other pointed instrument, write a name, or trace any outline through the wax, so as to expose a portion of the glass. Lay the etching, face downward, upon a bowl or trough of sheet-lead, in which has been placed a teaspoonful of powdered fluor-spar and enough strong sulphuric acid to convert it into a thin paste.

Cover the glass and the top of the dish with a sheet of paper and then gently heat the leaden vessel for a few moments, taking care not to melt the wax; then set the dish aside in a warm place and leave it at rest during an hour or two. Finally, melt the wax and wipe it off the glass with a towel or bit of paper; the glass will be found to be etched and corroded at the places where it was laid bare by the removal of the wax.

CHAPTER IX.

OZONE.

101. Besides ordinary **oxygen**, such as is found in the air and has been prepared in **Exps. 3** and **4**, another kind or form of this element is known to chemists. This new modification of oxygen has received a special name, and is called **ozone.**

Several other **elements**, notably **sulphur, phosphorus** and **carbon**, occur, as oxygen does, in very unlike states, or with very different attributes, while the fundamental chemical identity of the substance is preserved. The word **allotropism** is employed to express this capability of some of the elements : it is derived from Greek words signifying *of a different habit or character*. This word serves merely to bring into one category a considerable number of conspicuous facts, of whose essential nature we have no knowledge ; there is, of course, no virtue in the word itself to explain or account for the phenomena to which it refers.

102. **Ozone** is an exceedingly energetic chemical agent which resembles **chlorine** in some respects : it can therefore be advantageously studied in connection with the chlorine group.

It was long ago noticed that when an electrical machine was put in operation a peculiar, pungent odor was developed. More recently it has been observed that the same odor is manifested during the electrolysis of water (§ **25**), and that this odor resembles that evolved by moistened phosphorus when exposed to the air. It has gradually been made out, that the odor in each of these cases is due to the presence of a peculiar modification of oxygen, called **ozone** from a Greek word signifying to smell.

103. **Ozone** may be best prepared by certain electrical machines devised for the purpose ; but the phosphorus method will usually be found most convenient.

Exp. 42. – In a clean bottle of 1 or 2 litres' capacity place a piece of phosphorus 2 or 3 c. m. long, the surface of which has been scraped clean (under water) with a knife ; pour water into the bottle until the phosphorus is half covered ; close the bottle with a loose stopper, and set it aside in a place where the temperature is 20° or 30°. In the course of ten or fifteen minutes a column of fog will be seen to rise from that portion of the phosphorus which projects above the water : the original garlic odor of the phosphorus will soon be lost, and the peculiar odor of ozone will gradually pervade the bottle. After one or two hours, the bottle will be found to contain an abundance of ozone for purposes of illustration.

The chemical changes which occur during this experiment are complicated ; it will be enough to say of them that the phosphorus unites with oxygen from the air in the bottle to form an **oxide** of **phosphorus**, that during this process of **oxidation** a portion of the oxygen in the bottle is changed into **ozone**, and that some of the **ozone** remains, even after several hours, diffused in the air of the bottle.

It must be distinctly understood that only a very minute quantity of ozone is obtained in the foregoing experiment ; but ozone is a substance possessing great chemical power, and but little of it is needed in order to exhibit its characteristic properties.

104. **Ozone** is an irritating, poisonous gas : air which is highly charged with it is irrespirable, and produces effects on the human subject similar to those produced by chlorine. Its odor, which has been compared to that of weak chlorine, is so powerful that it can be recognized in air containing only one-millionth part of the gas. Like chlorine, ozone bleaches and destroys vegetable coloring matters, and is a powerful disinfectant. Like chlorine, it instantly decomposes the iodides of the metals ; upon this property is based a ready method of testing for its presence.

Exp. 43. — Into the bottle of ozonized air (Exp. 42), thrust a moistened slip of test-paper, saturated with starch and iodide of potassium, prepared as described in § 93 : the paper will instantly acquire a deep blue tint.

As in the case where the test-paper is employed for detecting chlorine (§ 93), so here, the reaction depends upon the displacement of the chemically feeble iodine by the more powerful ozone : —

$$2KI + O = K_2O + 2I.$$

The ozone here acts as oxygen, in one sense : at all events, the potassium oxide formed is not to be distinguished from potassium oxide prepared with common oxygen ; but this in no wise contradicts the fact that ozone is an extraordinarily active and energetic variety of oxygen, inasmuch as common oxygen will not effect this decomposition.

105. The great difference between ordinary oxygen and the allotropic modification, ozone, is generally explained by supposing that while the molecules of oxygen and the molecules of ozone are both made up of oxygen atoms, the former contains two atoms in each molecule (see page 90), while the latter contains three atoms. This idea is strengthened by the fact that when oxygen is converted into ozone a condensation takes place, and when the ozone is reconverted into ordinary oxygen there is an expansion to the original bulk. Other observed facts lead to the same conclusion, and the action of ozone on potassium iodide would probably be more correctly expressed by this equation :

$$2KI + O_3 = K_2O + 2I + O_2.$$

106. The **oxidizing power** of ozone is intense. When moisture is present, it oxidizes all the metals excepting gold, platinum and the platinum metals : even silver is oxidized by it at the ordinary temperature, and becomes covered with a brown coating of an oxide of silver. In like manner, most organic substances are quickly oxidized by ozone : when substances such as saw-dust, garden-mould, powdered charcoal, milk or flesh, are thrown into a bottle of ozonized air, the odor of ozone instantly disappears.

By virtue of this strong **oxidizing** power, ozone is of great importance as a **disinfecting agent.** It destroys instantly a multitude of offensive gases, such as arise from decaying animal and vegetable matter, and has been frequently recommended of late as a substance well fitted for the purification of sick-rooms and hospital-wards.

107. A minute proportion of ozone seems to exist in normal atmospheric air: it is especially abundant after a thunder-storm. It is seldom found in the air of thickly inhabited localities. At temperatures above 100° ozone is converted into ordinary oxygen.

108. **Antozone.** During the oxidation of phosphorus in moist air, Exp. 42, it was no doubt noticed that the bottle became filled with white fumes. Also in Exp. 7, § 17, during the rapid oxidation of phosphorus there was produced a white mist of considerable permanence, which remained long after the oxides of phosphorus, which were also formed, had been absorbed by the water. Moreover, if electrized oxygen (or electrized air) be passed through a solution of potassium iodide, the ozone will be completely removed; if, subsequently, the air or oxygen be allowed to bubble through water, the same peculiar mist will be formed. It was for a time supposed that this mist was caused by the presence of a third modification of oxygen, called **antozone**, which was supposed to be produced simultaneously with ozone by electrical action, and by processes of oxidation. Later research has, however, disproved the existence of such a third modification, and although it is impossible at present to account for all the effects which have been ascribed to antozone, in many cases they seem to be due to the presence of **hydrogen peroxide**, an oxide of hydrogen having the symbol H_2O_2.

CHAPTER X.

SULPHUR, SELENIUM AND TELLURIUM.

SULPHUR (S).

109. **Sulphur** occurs somewhat abundantly in nature both in the free state and in combination with other elements. Many ores of metals, for example, are sulphur compounds. It is a component of several abundant salts, such as the sulphates of calcium, barium and sodium, and occurs in small proportion in many animal and vegetable substances. Free sulphur is found

chiefly in volcanic districts. Generally it occurs mixed with earthy matters, but it often forms distinct veins, and is sometimes found in the shape of well-defined crystals of considerable size. At the present time about nine-tenths of the sulphur of commerce comes from Sicily.

Native sulphur is usually subjected to a rough purification at the place of its occurrence. This purification is sometimes effected by distilling the volcanic earth in retorts or jars of earthenware ; or, if the earth be very rich in sulphur, it is simply heated in large kettles and the melted sulphur dipped off from above, while the earthy impurities settle to the bottom of the kettle : sometimes the sulphur is piled up in heaps, or in kilns, and set on fire, a portion of the sulphur in burning furnishing the heat by which the rest of the sulphur is melted : the melted sulphur flows out from the mass, and is collected in receivers. As the crude sulphur comes to us, it is in irregular lumps of a dirty light-yellow color, and is largely employed for manufacturing purposes. It is purified by being distilled from iron retorts into large chambers constructed of masonry, in which it is deposited either in the form of a light powder, known as flowers of sulphur, or in the liquid state, according to the temperature of the chambers.

110. At the ordinary temperature of the air, **sulphur** is a brittle solid of a peculiar light-yellow color. It has neither taste nor smell, excepting that when rubbed it exhales a faint and peculiar odor. Most of the odors which in every-day life are referred to sulphur are really the odors of various compounds of sulphur, and are not evolved by the element itself. The symbol of sulphur is **S** : its atomic weight is 32, being precisely twice as great as the atomic weight of oxygen.

111. **Sulphur** behaves in a very remarkable manner on being heated. When melted at the lowest possible temperature, 100° to 115°, it forms a limpid liquid of a light-yellow color ; but, if this liquid be heated more strongly, it begins to become viscid and dark-colored at about 150°, and at 170° to 200° it is almost black, and at the same time so thick and tenacious that it can not be poured from the vessel which holds it, even if the vessel be inverted. At 330° to 340° it regains its fluidity in part, though the liquid is still dark-colored, and finally, at about

440°, it begins to boil, and is converted into an amber-colored vapor. The specific gravity of sulphur vapor, referred to hydrogen, is 32.

112. If melted sulphur in the viscid state, or, better, that which has regained its mobility, be suddenly cooled, a semi-solid modification of sulphur, remarkably different from the ordinary form, will be obtained.

Exp. 44. — Place in a test-tube, of about 30 c. c. capacity, 15 to 20 grms. of coarsely-powdered sulphur ; melt the sulphur slowly over the gas-lamp, and continue to heat it until it begins to boil, noting, meanwhile, the changes which the sulphur undergoes, — as described in § 111. Finally, pour the hot sulphur, in a fine stream, into a large dish full of cold water. There will be obtained a soft, elastic, reddish-brown mass, which can be kneaded and moulded like wax, and drawn out into threads like caoutchouc.

Fig. 24.

This **soft sulphur** can not be preserved for any great length of time ; it slowly hardens and changes into ordinary brittle yellow sulphur.

113. **Sulphur** may readily be obtained in the form of crystals.

Exp. 45. — In a small beaker glass, or porcelain capsule, slowly heat 50 to 60 grms. of sulphur until it has entirely melted. Remove the vessel from the lamp, and allow it to cool slowly until about a quarter part of the sulphur has solidified ; then pour off into a basin of water that portion of the sulphur which is still liquid, breaking through, for this purpose, the crust at the top of the liquid, if any such have formed. The interior of the vessel will be found to be lined with transparent crystals.

Exp. 46. — In a test-tube, melt enough sulphur to fill one-quarter of the tube ; place the tube in such a position that its contents may cool slowly and quietly, and then watch the formation of crystals as they shoot out from the comparatively cold walls of the tube towards the centre of the liquid.

Exp. 45 represents one general method of obtaining crystals. Crystals of many of the metals, lead and bismuth for example, can be obtained in a similar manner : it is only necessary to perform the operation in a crucible of some refractory material, placed in a furnace.

Exp. 46, besides illustrating the manner in which crystals form, teaches us something of the physical structure of solid bodies. The solid mass of sulphur which is left in the test-tube, when it has become cold, is evidently nothing more than a compact bundle of interlaced crystals : it possesses what is called a **crystalline structure.** This crystalline structure is apt to render a body brittle : substances which possess it are liable to break " with the grain," or to split in certain directions determined by the shape of the crystals, and called lines of **cleavage :** a stick of roll-brimstone, for example, may be readily broken or cut across, but not so easily in the direction of its length.

114. Another easy way to crystallize sulphur is by the method of solution and evaporation, such as was employed in the preparation of **potassium nitrate** (**Exp. 25**). Sulphur is not soluble in water, but it dissolves readily in a liquid compound of sulphur and carbon, known as carbon bisulphide, which, being readily volatile, quickly escapes, on exposure to the air, and so deposits the sulphur. The crystals thus obtained differ in shape from those obtained by the method of fusion.

Although thousands of crystal-forms occur in nature or have been produced by art, it has been found possible to refer these forms to six general classes called systems of crystallization. It is true of almost all chemical substances which can be obtained in crystals, that while the individual crystals may vary somewhat in form, all the forms in which the substance occurs are such as may be referred to one and the same system. In the case of sulphur, however, the crystals obtained by the method of fusion, and those obtained by the method of solution, must be referred to two entirely distinct systems. There are other substances besides sulphur which present this same phenomenon. Substances which are thus capable of assuming crystalline forms

belonging to two different systems are said to be **dimorphous** (two-formed).

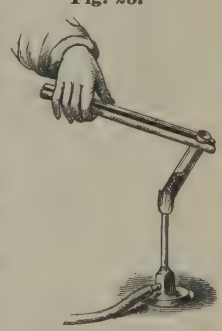
The two varieties of sulphur differ considerably in various physical properties. One variety may, however, be converted into the other, and their chemical composition is identical. Each is sulphur, and nothing more. The amorphous "soft sulphur" obtained in Exp. 44 may be regarded as a third modification of sulphur.

Crystals of sulphur of large size and great beauty occur in Nature, and are supposed to have been formed by sublimation, *i. e.*, the sulphur has been converted into vapor, and the vapor cooled very slowly. The method is hardly practicable in the laboratory, although crystals have been formed artificially in this way.

115. Sulphur unites energetically with most of the other elements, such union being, in many cases, attended with evolution of light. Most of the metals, for example, combine with it directly, just as they do with oxygen.

This has already been illustrated in the case of copper by Exp. 1, § 2. The product of this reaction was copper sulphide; and, in general, compounds of sulphur with the metallic elements are called **sulphides**.

Fig. 25.



Exp. 47. — Mix intimately 4 grms. of flowers of sulphur and 7 grms. of the finest iron filings. Place the mixture in an ignition-tube 10 to 12 c. m. long, and heat the lower end of the tube over the gas-lamp. In a short time the mass will begin to glow, as the sulphur and iron enter into chemical combination, and this ignition will, of itself, pass through the entire length of the tube, even if the lamp be withdrawn. The final product of the reaction is iron sulphide.

116. **Sulphur** unites readily with oxygen at a comparatively low temperature. When heated in the air, it takes fire at about 250°, and burns with a peculiar blue light. The irritating, suffocating gas, which is produced, will be shortly described under the name of **sulphurous anhydride.**

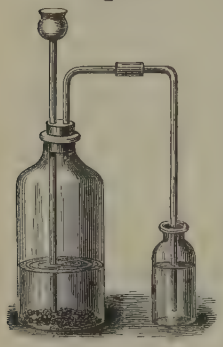
The use of sulphur on ordinary matches depends on the low tem-

perature at which it takes fire. Being ignited by the burning phosphorus, it burns until the less readily combustible wood is set on fire.

117. **Hydrogen sulphide** (H_2S) or **sulphuretted hydrogen,** as it is often called, is a colorless gas which smells like rotten eggs. It may be conveniently prepared by treating iron sulphide with dilute chlorhydric acid.

Exp. 48. — In a gas-bottle, Fig. 26, put 10 or 12 grms. of iron sulphide (see Exp. 47) ; replace the cork in the bottle and introduce the gas delivery-tube into another small bottle containing cold water, letting it dip 5 or 6 c. m. beneath the surface of the water. Through the thistle-tube, pour into the gas-bottle water enough to seal the lower extremity of this tube : then add, through the thistle-tube as before, 2 or 3 teaspoonfuls of strong chlorhydric acid, and observe that bubbles of gas soon begin to pass through the water in the absorption bottle.

Fig. 26.



Hydrogen sulphide is soluble in water to a considerable extent, and is consequently taken up by the water in the absorption bottle. The solution thus obtained, known as sulphuretted-hydrogen-water, is much employed as a reagent in chemical laboratories.

When the disengagement of gas slackens, a new portion of chlorhydric acid may be added through the thistle-tube, and this process continued until the water in the absorption bottle smells strongly of the gas.

This experiment should be performed out of doors, or in a draught of air so arranged that those portions of the gas which escape solution shall be carried away from the operator.

The reaction which takes place may be represented as follows : —

$$FeS + 2HCl = FeCl_2 + H_2S.$$

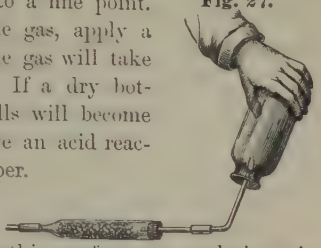
118. **Hydrogen sulphide** is readily inflammable. It burns with a blue flame, producing water and sulphurous acid gas : —

$$H_2S + 3O = H_2O + SO_2.$$

Exp. 49. — To the delivery-tube of the gas-bottle employed in generating hydrogen sulphide, attach a drying-tube containing

fragments of calcium chloride, and with the tube connect a piece of No. 6 glass tubing drawn out to a fine point. When the apparatus is full of the gas, apply a match to the end of the tube. The gas will take fire, and burn with a blue flame. If a dry bottle be held over the flame, the walls will become coated with moisture which will have an acid reaction and will redden blue litmus paper.

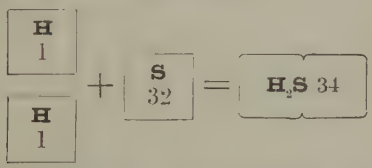
Fig. 27.



The jet of hydrogen sulphide should not be lighted until all the air is expelled from the apparatus, as this gas forms an explosive mixture with air.

119. **Hydrogen sulphide** is readily decomposed by heat, as may be shown by passing a current of the gas through a glass tube, heated for a portion of its length. The gas will be separated into hydrogen and sulphur: the latter will be deposited on the cold portion of the tube.

Analysis has proved that the composition of **hydrogen sulphide,** both by volume and by weight, may be expressed by the following diagram, in which the symbol **S** represents a unit volume of sulphur in the state of vapor.



120. **Hydrogen sulphide** is very poisonous: when respired in the pure state, it quickly proves fatal, and it is very deleterious, even though largely diluted with atmospheric air. It is therefore best, when experimenting with it, to operate where there is a free circulation of air.

The gas exists as a natural constituent of some mineral waters which are thence called sulphurous, such as the Virginia Sulphur Springs, and the mineral springs at Sharon, N. Y. It is also found in the air and water of foul sewers, and wherever animal matter is undergoing putrefaction.

121. When moist **hydrogen sulphide** comes in contact with certain of the metals, it is decomposed.

Exp. 50.— Place a drop of sulphuretted-hydrogen-water (Exp. 48) upon a bright piece of copper, lead or silver. The metal will quickly become black. The sulphur of the hydrogen sulphide unites with the metal, to form a sulphide of the metal, while the hydrogen escapes, or we may say that the metal *replaces* the hydrogen in the hydrogen sulphide.

$$Cu + H_2S = CuS + 2\,H.$$
$$2\,Ag + H_2S = Ag_2S + 2\,H.$$

From a solution of any compound of these metals, hydrogen sulphide will throw down the sulphide of the metal.

Exp. 51. — Dissolve a small crystal of lead nitrate in a test-tube half full of water, and to this solution add a few drops of the sulphuretted-hydrogen-water. Lead sulphide is thrown down as a black precipitate, and nitric acid is set free.

$$PbN_2O_6 + H_2S = PbS + 2\,HNO_3.$$

On account of this property of precipitating various metallic sulphides, hydrogen sulphide is much used in the chemical laboratory as a reagent.

122. **Sulphur and Oxygen.** — Of the compounds of sulphur and oxygen the most important are **sulphurous anhydride** and **sulphuric anhydride.**

123. **Sulphurous anhydride** (SO_2), commonly called **sulphurous acid** (see § **63**). — This is the only one of the various compounds of oxygen and sulphur which can be formed by the direct union of its constituents. It is produced whenever sulphur is burned in air or in oxygen gas.

Fig. 28.

Exp. 52. — Light a piece of sulphur in a deflagrating spoon, and suspend the latter in a half-litre bottle full of air. On examining the contents of the bottle, after the sulphur has ceased to burn, there will be found an irritating, suffocating gas having the peculiar odor which is familiar as that of a burning match. The bottle is now full of sulphurous anhydride, mixed with the nitrogen originally present in the air.

An easier method of preparing pure **sulphurous acid** is by depriving common sulphuric acid of part of its oxygen.* This can be effected by a variety of reducing or deoxidizing agents. For example, when concentrated sulphuric acid is heated with metallic copper, there is formed a sulphate of the metal, water and sulphurous acid :—

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

Certain other metals, such as mercury, for example, can be employed instead of copper, the reaction being precisely similar.

124. **Sulphurous acid** is a transparent and colorless gas. It is irrespirable and suffocating, and when mixed with air, even in small proportion, occasions violent coughing. It is not inflammable, but, on the contrary, it stops combustion.

The flame of a taper is immediately extinguished on being immersed in sulphurous acid gas, just as it is by nitrogen. A useful application of this property of the gas is in extinguishing burning chimneys. A handful of fragments of sulphur being thrown upon the hot coals in the grate, and the openings of the fireplace being closed in such manner that no air shall enter the chimney, excepting that which passes through the fire, the chimney will quickly become filled with an atmosphere of sulphurous acid mixed with nitrogen from the air employed in burning the sulphur, and the burning soot upon the walls of the chimney will be immediately extinguished.

It is, of course, essential that the chimney should then be closed at the top, so that air may be excluded and the chimney kept full of the fire-extinguishing atmosphere until its walls shall have cooled to below the kindling temperature of the soot.

125. **Sulphurous anhydride** can readily be obtained in the liquid state by passing the gas through a U-tube immersed in a freezing-mixture of ice and salt. On being exposed to the air at ordinary temperatures, this liquid evaporates with great rapidity, and consequently occasions very intense cold.

* The substances now designated as **anhydrides** were formerly called **acids**, as stated in § 63. In the case of sulphurous, arsenious and carbonic anhydrides, the popular names sulphurous, arsenious and carbonic acids have such currency that they will be employed in this Manual where no ambiguity can arise from such use.

If a quantity of the liquid be poured into water, the temperature of which is a few degrees above 0°, a portion will evaporate at once, another portion will dissolve in the water and a third portion of the heavy oily liquid will sink to the bottom of the vessel. If the portion which has thus subsided be stirred with a glass rod, it will boil at once, and the temperature of the water will be so much reduced that a portion, or even the whole, of the water will be frozen.

The volumetric composition of **sulphurous anhydride** is 1 volume of sulphur vapor and 2 volumes of oxygen condensed to 2 volumes of the compound gas. The gas is very readily soluble in water, and may be regarded as combining with a portion of the water to form sulphurous acid, the formula of which would be H_2SO_3. The term "sulphurous acid" is, however, ordinarily used to denote the gas SO_2.

126. An important property of **sulphurous acid** is its power of **bleaching** vegetable colors. It is extensively employed in bleaching articles of straw, wool, silk, etc., which would be injured by chlorine. The bleaching may be effected by immersion in the aqueous solution of sulphurous acid or by exposure to the fumes of burning sulphur. In the latter case the articles to be bleached must be moistened. The dry anhydride does not bleach. In most cases sulphurous acid does not destroy the coloring matters as chlorine does, but seems to combine with them to form colorless compounds. These colorless compounds can be broken up, with restoration of color, by exposing them to the action of various chemical agents capable of setting free sulphurous acid.

Exp. 53. — Bleach a red rose by hanging it in a bottle in which sulphur has been burned, or by holding it over burning sulphur. Immerse the bleached rose in dilute sulphuric acid, dry and warm it, and observe that the color will re-appear.

In the arts, the process of bleaching is usually conducted in large chambers, in which the slightly moistened articles are hung while sulphur is burned below. The damp goods absorb the gas and gradually become white. A practical illustration of the restoration of color by chemical agents is seen in the reproduction of the original yellow color of the wool when new flannel is washed. The alkali of the soap removes the sulphurous acid, and the color re-appears.

127. **Sulphuric anhydride** (SO_3) may be prepared by the direct oxidation of **sulphurous anhydride.** If a mixture of sulphurous anhydride and oxygen be passed over heated, very finely divided platinum (platinum sponge), the two gases unite to form **sulphuric anhydride,** which condenses in the cooled receiver. It is a white, waxlike solid, crystallizing in silky fibres, resembling asbestos. If a bit of it be thrown into water, the water hisses as if a hot iron had been thrust into it; and the sulphuric anhydride unites with a portion of the water with the evolution of great heat to form **sulphuric acid.** The solid anhydride has so great an attraction for water, that it can be preserved only in dry tubes sealed at the lamp.

128. **Sulphuric acid** (H_2SO_4) is one of the most important products of chemical manufacture, and is made in enormous quantities. In the same way that the metal iron may be said to be the basis of all mechanical industries, sulphuric acid lies at the foundation of the chemical arts. By means of sulphuric acid, the chemist either directly or indirectly prepares almost every thing with which he has commonly to deal.

129. **Sulphuric acid** is made by oxidizing sulphurous acid. This oxidation cannot be effected *directly* in any economical manner; it is necessary to use some **oxidizing agent.**

This term **oxidizing agent** is applied to a substance which habitually and readily imparts oxygen to other bodies with which it is brought in contact: on the other hand, a substance which habitually and readily takes oxygen out of other substances with which it is brought in contact is called a **reducing agent.*** Nitric acid, such as was prepared in Exp. 22, § 59, is a very powerful oxidizing agent, and sulphuric acid might be made by boiling sulphur for a long time in nitric acid. This method would, however, not be practicable on a large scale. Nitric acid also oxidizes sulphurous acid.

Exp. 54.—Charge a bottle, of the capacity of a litre or more, with sulphurous acid by burning in it a bit of sulphur. Fasten a shaving, or, better, a tuft of gun-cotton, upon a glass rod or tube bent at one end in the form of a hook; wet the shaving in concentrated nitric acid, and hang it in the bottle of sulphurous acid. Red fumes of

* The terms oxidizing agent and reducing agent are often employed in a much wider sense than here implied. See page 290.

nitrogen peroxide will immediately form about the nitric acid, and will gradually fill the bottle. The appearance of the red fumes (nitrogen peroxide) shows that there has been a loss of oxygen on the part of the nitric acid. The reaction may be thus written : —

$$2\,HNO_3 + SO_2 = H_2SO_4 + 2\,NO_2.$$

In this case sulphurous acid is an example of a reducing agent. Sulphurous acid in the presence of much moisture can take oxygen from all the higher oxides (and acids) of nitrogen, as HNO_2, NO_2, and HNO_3, and reduce them all to nitric oxide, NO.

130. The method employed in the actual preparation of **sulphuric acid** upon the large scale depends upon the fact illustrated in the last experiment.

Fig. 29.

Fig. 29 shows, in a rough and very general way, the manner in which the manufacture is conducted. The sulphurous acid is obtained by burning crude sulphur or, more commonly, a compound of sulphur and iron, known as iron pyrites, in properly-constructed furnaces. The gas, together with a large excess of atmospheric air, is then conducted into the first of a series of enormous chambers, into which jets of steam are constantly blowing : these chambers are constructed of sheet-lead, a metal on which cold sulphuric acid has little action. Nitrous fumes are supplied either by allowing nitric acid to fall in fine streams through the incoming current of sulphurous acid and air, or from the decomposition of sodium nitrate by means of sulphuric acid, this decomposition taking place in an iron pot heated by the burning sulphur.

In conformity with the principles above stated, the SO_2 in contact with the steam, reacts upon the nitrous fumes : there is formed sulphuric

acid, which condenses upon the sides of the chamber and trickles down to the floor, and nitric oxide. But, as there is present in the chamber an excess of air, the **NO** immediately unites with a portion of the oxygen therein contained, and is converted into NO_2. This NO_2 immediately reacts upon a new portion of SO_2, and the process thus goes on through a whole series of leaden chambers, the very small portion of nitric acid at first taken being sufficient to prepare a large quantity of sulphuric acid. In reality, the oxygen employed in converting the sulphurous into sulphuric acid all comes from the air, excepting a very little at first : the nitrous fumes serve only as a conveyer of oxygen. The **NO** takes oxygen from the air and transfers it to the sulphurous acid, which is, by itself and unaided, incapable of combining with oxygen. It will, of course, be understood, that although we trace out these reactions as if they were consecutive, they are really, so far as we know, simultaneous.

Theoretically, a single portion of nitric acid would be sufficient to effect the conversion of an unlimited amount of sulphurous into sulphuric acid, but practically this power is qualified by a variety of circumstances. It is found to be impossible, for example, to introduce new portions of air into the mixture of sulphurous acid and nitric oxide for an indefinite period ; for, at a certain point, these gases become so loaded down with nitrogen derived from the air already consumed, that they are as good as lost in it. In general, the flow of gases is so regulated that all the sulphurous acid shall be oxidized, and that nothing but nitric oxide and the waste nitrogen shall pass out of the last leaden chamber.

131. The acid obtained in the lead chambers as described above is very dilute. It is concentrated by evaporating it, first in leaden pans, and finally in large glass retorts or in platinum stills, until it has nearly the composition H_2SO_4.

The acid thus boiled down is the concentrated sulphuric acid, or **oil of vitriol,** of commerce ; its specific gravity is usually about 1.83, that of the absolutely pure acid being 1.842. Besides this slight excess of water, it contains also, in solution, a certain quantity of lead sulphate, and a variety of other impurities. For most purposes, however, it will answer as well as the pure acid. Like the latter, it is a heavy, oily, colorless and odorless liquid, boiling at about 330°.

132. At the ordinary temperature, sulphuric acid does not

vaporize, but, on the contrary, greedily absorbs water from the air, and so increases in bulk. In moist weather, its bulk may increase to the extent of a quarter or more, in the course of a single day, and, by longer exposure, a still larger quantity of water will be taken up; the acid must always be kept, therefore, in tightly-stoppered bottles.

Sulphuric acid unites with liquid water, with great energy, much heat being evolved at the moment of combination: during the union a certain amount of condensation occurs, the mixture, when cold, occupying less space than was previously occupied by the acid and the water. The water and acid may be mixed in all proportions, being mutually soluble one in the other.

In mixing water and sulphuric acid, the acid should always be poured into the water, in a fine stream, not the water into the acid, — the water being meanwhile stirred. In this way the heavy acid has an opportunity to mix with the water as it sinks down through it. If, by any accident, water were to fall upon sulphuric acid, it would float on top of it, and great heat would be developed at the point of contact of the two liquids: if the quantities of acid and water were large, sudden bursts of steam would be occasioned, and serious damage might arise from the scattering about of portions of the acid.

Exp. 55. — Place in a beaker glass of about 250 c. c. capacity, 30 c. c. of water; in accordance with the directions above given, pour into the water 120 grms. of concentrated sulphuric acid, and stir the mixture with a narrow test-tube containing a teaspoonful of water. So much heat will be evolved during the union of the water and the acid that the water in the test-tube will boil.

133. **Sulphuric acid** is one of the most powerful acids known. When diluted with a thousand times its bulk of water, it is still capable of reddening blue litmus. It sets free most of the other acids from their salts, in the same way that we have seen it set free nitric acid from sodium nitrate in **Exp. 22, § 59.** It is intensely caustic and corrosive, and quickly chars and destroys most vegetable and animal substances.

Exp. 56. — Into a test-glass pour a table-spoonful of sulphuric

acid and immerse in it a splinter of wood. The wood will blacken as if charred by fire, and the acid will become dark-colored. Wood is composed of carbon, hydrogen and oxygen, and since sulphuric acid unites with compounds of hydrogen and oxygen, rather than with carbon, a portion of the latter is left free; some carbonaceous matter is, however, dissolved by the acid and darkens it. The acid of commerce is often dark-colored from fragments of straw or other organic matter having accidentally fallen into it.

134. **Sulphates.** — If the hydrogen of sulphuric acid be replaced by various metals, a class of bodies is formed called **sulphates**: thus, Na_2SO_4 is sodium sulphate; $CaSO_4$ is calcium sulphate, etc.

In the formation of the sulphates of those metals which replace hydrogen atom for atom (§ 74), it is not necessary that both atoms of hydrogen in the sulphuric acid, H_2SO_4, should be replaced. We may, for example, have a compound in which sodium replaces only one of the hydrogen atoms; namely, $HNaSO_4$, hydrogen sodium sulphate. Acids like sulphuric acid, which have two replaceable hydrogen atoms, are called **bi-basic**.

135. **Fuming Sulphuric Acid.** — Sulphuric acid was formerly made by distilling in earthen retorts the salt now known as ferrous sulphate, formerly called green vitriol. Hence the origin of the name oil of vitriol, which, in England and this country, has come to be applied solely to the common acid, H_2SO_4. The acid thus obtained is a dense fuming liquid, which may be regarded as sulphuric anhydride dissolved in sulphuric acid. It is used principally for dissolving indigo, a certain quantity being still made for this purpose.

There are other well-defined compounds of oxygen and sulphur. They, are, however, of much less importance, and are of little interest in an elementary manual.

SELENIUM (Se) AND TELLURIUM (Te).

136. These elements are rare, and of little or no industrial importance; but to the chemist they are exceedingly interesting on account of the close resemblance they bear to sulphur. The three elements sulphur, selenium and tellurium, constitute a group which is equally

remarkable with that formed by chlorine, bromine and iodine. (See § 97.)

137. **Selenium** is never found in any considerable quantity in any one place. Traces of it occur in many varieties of native sulphur and in various metallic sulphides. In its properties and in its chemical behavior, selenium resembles sulphur in many respects, while, in others, it is like tellurium. Like sulphur and oxygen, it occurs in distinct **allotropic** modifications (§§ 101, 114): it forms with hydrogen a compound, hydrogen selenide (H_2Se), resembling hydrogen sulphide: it forms an acid, selenic acid (H_2SeO_4), resembling sulphuric acid. There are selenates possessing characters similar to the sulphates, and crystallizing in the same form; and, according to a principle illustrated by the chlorine group, selenium, which has the higher atomic weight (79.5), is a weaker chemical agent than sulphur (32).

138. **Tellurium** occurs in nature even more rarely than selenium: sometimes it is found in the free state, but more generally in combination with the heavy metals, such as gold, silver, lead, copper and bismuth. Tellurium is of a silver-white color and glittering metallic lustre. In many of its physical characters it would seem to be allied to certain metals, but its chemical properties place it in the same group with sulphur and selenium. It forms compounds with hydrogen, oxygen and with other elements which resemble the corresponding sulphur compounds. Its atomic weight is 128.

The elements sulphur, selenium and tellurium in their chemical properties are closely allied to oxygen. Attention has already been called to the resemblance of the compounds of selenium and tellurium to those of sulphur. The formulæ of a few of these compounds are here given to bring the matter more clearly before the eye.

Water.	Hydrogen sulphide.	Hydrogen selenide.	Hydrogen telluride.
H_2O	H_2S	H_2Se	H_2Te
Iron oxide.	Iron sulphide.	Iron selenide.	Iron telluride.
FeO	FeS	FeSe	FeTe
Ether (Ethyl oxide).	Ethyl sulphide.	Ethyl selenide.	Ethyl telluride.
$(C_2H_5)_2O$	$(C_2H_5)_2S$	$(C_2H_5)_2Se$	$(C_2H_5)_2Te$
Alcohol (Ethyl hydrate).	Mercaptan (Ethyl Hydrogen sulphide).	Selenium mercaptan.	Tellurium mercaptan.
$(C_2H_5)HO$	$(C_2H_5)HS$	$(C_2H_5)HSe$	$(C_2H_5)HTe$

CHAPTER XI.

COMBINATION BY VOLUME.

139. A comparison of the formulæ representing the **volumetric composition** of all the well-defined compound gases and vapors which have been thus far studied, will bring into clear view some of the general facts relating to **combination by volume.**

It has been established, by experiment, that the following compounds are formed by the chemical union, without condensation, of equal volumes of the two elements which enter into each compound :—

Hydrogen 1 vol.	+	Chlorine 1 vol.	=	Chlorhydric Acid 2 vols.	, or	H 1	+	Cl 35.5	=	HCl 36.5
Hydrogen 1 vol.	+	Bromine 1 vol.	=	Bromhydric Acid 2 vols.	, or	H 1	+	Br 80	=	HBr 81
Hydrogen 1 vol.	+	Iodine 1 vol.	=	Iodohydric Acid 2 vols.	, or	H 1	+	I 127	=	HI 128
Nitrogen 1 vol.	+	Oxygen 1 vol.	=	Nitric oxide 2 vols.	, or	N 14	+	O 16	=	NO 30

It has further been found that the following compounds of two elements contain two volumes of one element and one volume of the other, but that these three volumes are condensed during the act of combination into two volumes :—

Hydrogen 2 vols.	+	Oxygen 1 vol.	=	Steam 2 vols.	, or	H_2 2	+	O 16	=	H_2O 18
Hydrogen 2 vols.	+	Sulphur 1 vol.	=	Hydrogen Sulphide 2 vols.	, or	H_2 2	+	S 32	=	H_2S 34
Nitrogen 2 vols.	+	Oxygen 1 vol.	=	Nitrogen Protoxide 2 vols.	, or	N_2 28	+	O 16	=	N_2O 44
Nitrogen 1 vol.	+	Oxygen 2 vols.	=	Nitrogen Peroxide 2 vols.	, or	N 14	+	O_2 32	=	NO_2 46
Sulphur 1 vol.	+	Oxygen 2 vols.	=	Sulphurous Anhydride 2 vols.	, or	S 32	+	O_2 32	=	SO_2 64

To this list must be added hydrogen selenide (H_2Se), hydrogen telluride (H_2Te), selenious anhydride (SeO_2) and tellurous anhydride (TeO_2).

Lastly, still a third mode of combination by volume with condensation of four volumes to two occurs in the two following cases: —

Nitrogen 1 vol.	+	Hydrogen 3 vols.	=	Ammonia 2 vols.	, or	**N** 14	+	$\mathbf{H_3}$ 3	=	$\mathbf{NH_3}$ 17
Sulphur 1 vol.	+	Oxygen 3 vols.	=	Sulphuric Anhydride 2 vols.	, or	**S** 32	+	$\mathbf{O_3}$ 48	=	$\mathbf{SO_3}$ 80

In all these cases, the **unit-volume** is, of course, the same for every element and compound; what the absolute bulk of this unit-volume may be, is not an essential point, for the relations remain the same, whatever the unit of measure. Three **condensation-ratios** are thus exhibited: first, a condensation of 0; second, one of $\frac{1}{3}$; and third, one of $\frac{1}{2}$. The space occupied by the compound molecule is, in each case, exactly twice the unit-volume.

The examples just given, although including all the compounds which we have yet studied, are only very few compared with the vast number of gaseous compounds which have been investigated, and where the same thing has been found to hold true. **Two volumes** of a compound gas invariably result from the chemical combination of one volume of hydrogen with one volume of chlorine, of two volumes of hydrogen with one volume of oxygen, of three volumes of hydrogen with one volume of nitrogen, and so on. This doubled volume is often called the **normal** or **product-volume** of a compound gas.

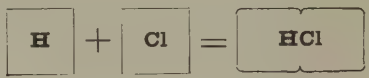
If, in considering the compounds already mentioned in this chapter, we choose for our unit-volume the space occupied by the atom of hydrogen in the molecule of chlorhydric acid (*i. e.*, in other words, the volume of the atom of hydrogen when not under condensation), we shall be led to very important theoretical results. For then our product volume will be in each case the space occupied by the molecule of the compound gas, and we shall be led to the conclusion that the space occupied by a single molecule of each of these gaseous compounds is the same. This is, indeed, believed to be true in the case of all gaseous molecules. In organic chemistry a great multitude of com-

pounds, many of them very complicated, have been investigated, and the same law has been found to hold good. The molecule of every compound in the gaseous state occupies a volume twice as large as that occupied by the atom of hydrogen.

Since, then, the molecule of a compound gas or vapor occupies two of these unit volumes, and the specific gravity of a gas or vapor is the weight of one unit-volume of that gas or vapor as compared with the weight of the same volume of hydrogen, it is obvious that the specific gravity of the gas or vapor may be found from the molecular weight by dividing the latter by two. *The specific gravity of a compound gas or vapor is, therefore, one-half its molecular weight.*

140. **Molecular condition of elementary gases.**—There are certain physical laws in regard to compressibility and expansion which govern all gases, and which are best explained by the hypothesis, usually spoken of as the **Law of Ampère**,—that *equal volumes of all gases, simple as well as compound, under like conditions of temperature and pressure, contain the same number of molecules.* Starting with this hypothesis, let us inquire what inferences we can draw with regard to the molecular condition of the elementary gases when in the free state. Suppose, then, we take any volume of hydrogen, the volume occupied by 1000 molecules, for example: an equal volume of chlorine will contain the same number of molecules. If the two gases be mixed and exposed to diffused sunlight they will combine without condensation to form chlorhydric acid. We shall then have two volumes of chlorhydric acid. According to the assumption just made that equal volumes of all gases contain the same number of molecules, each of these two volumes will contain 1000 molecules of the acid and the two volumes will contain 2000 molecules. Each molecule of the acid contains one atom of hydrogen and one atom of chlorine, hence in the two volumes of chlorhydric acid we shall have 2000 atoms of hydrogen and 2000 atoms of chlorine. These 2000 atoms of hydrogen (or chlorine) came from the one volume of the gas which we supposed to contain 1000 molecules; therefore, this volume contained at the same time 1000 molecules and 2000 atoms: hence each molecule must be made up of two atoms. It is clear that this train of reasoning is independent of the particular numerical value assumed as the number of molecules in the two volumes of chlorhydric acid. If, therefore,

the molecule of chlorhydric acid is represented by the formula **HCl**, and the diagram, —



there is good reason to assign to *free* hydrogen and *free* chlorine the formulæ **HH** and **ClCl**, or (H_2 and Cl_2), and to represent the constitution of all uncombined gases by such diagrams as

Upon these models the molecular formulæ of most of the elements with which we have become acquainted might readily be written. It is only in a *free* state that the elementary gases and vapors are thus conceived to exist as molecules ; when they enter into combination, it is by atoms rather than by molecules. An atom of hydrogen unites with an atom of chlorine : three atoms of hydrogen combine with one of nitrogen.

We may study the molecular condition of the elementary gases from another point of view. If the Law of Ampère be, as it is believed to be, true of *simple* as well as of compound gases, it will be true that the **vapor density** (or the specific gravity of the substance in the state of gas) is one-half the molecular weight, and, *vice versa*, that the molecular weight is twice the vapor density. If, now, the specific gravity of hydrogen be one, its molecular weight must be $2 \times 1 = 2$. If the molecule weigh 2 and the atom weigh 1, the unit of weight being the same in both cases, the molecule must contain 2 atoms. The same reasoning will hold in the case of the elementary gases, oxygen, chlorine, and nitrogen, also in the case of the elementary substances, bromine, iodine, sulphur, selenium, tellurium, sodium and potassium. which are not gases under ordinary atmospheric conditions, but which can be converted into gases at a higher temperature. As, for example,

	Vapor Density.	Molec. Weight. = V. D. × 2.	Atomic Wt.	No. of atoms in Molecule.
O	16	32	16	2
Cl	35.5	71	35.5	2
I	127	254	127	2
S	32	64	32	2

etc.

Of all the other elementary substances, four, namely, arsenic, phosphorus, mercury and cadmium, have been converted into vapor, and the specific gravity of their vapors determined. If we apply the same reasoning to them we find that the molecules of arsenic and phosphorus contain each four atoms, while the molecules of mercury and cadmium contain each a single atom only. It is probable that zinc should be classed with mercury and cadmium.

	Vapor Density.	Molec. Wt.	Atomic Wt.	No. of atoms in Molecule.
As	150	300	75	4
P	62	124	31	4
Hg	100	200	200	1
Cd	56	112	112	1

If this view of the molecular structure of free elementary gases and vapors be correct, perfect consistency would require that no equation should ever be written in such a manner as to represent less than a single molecule of an element in a free state as either entering into or issuing from a chemical reaction. Thus, instead of $2\,H + O = H_2O$, $N + 3\,H = NH_3$, $HCl + Na = NaCl + H$, it would be necessary to write $2\,H_2 + O_2 = 2\,H_2O$, $N_2 + 3\,H_2 = 2\,NH_3$, $2\,HCl + Na_2 = 2\,NaCl + H_2$.

We have not heretofore conformed to this theoretical rule, and do not propose to in the succeeding pages, and this for two reasons: first because many equations, representing chemical reactions, must be multiplied by two, in order to bring them into conformity with this hypothesis concerning molecular structure; the equations are thus rendered unduly complex; — secondly, because, in undertaking to make chemical equations express the molecular constitution of elements and compounds, as well as the equality of the atomic weights on each side of the sign of equality, there is imminent danger of taking the student away from the sure ground of fact and experimental demonstration, into an uncertain region of hypotheses based only on definitions and analogies; — thirdly, because we are ignorant of even

the probable molecular symbol of most of the elements. Of all the elementary substances recognized, we have reason to believe that eleven, when in the gaseous state, are made up of molecules containing each two atoms, that two contain four atoms, and that three contain only a single atom to the molecule. Of the molecular structure of the remaining elements, numbering three-fourths of the whole, we, at present, know nothing.

141. **Volumetric interpretation of symbols.**—This important matter forms the subject of § 517, page 291, but it should be studied as a part of the present chapter, as should also § 518, page 292.

CHAPTER XII.

PHOSPHORUS (P).

142. **Phosphorus** occurs somewhat abundantly and very widely diffused in nature. It is never found in the free state, but almost always in combination with oxygen and some one of the metals. The most abundant of its compounds is **calcium phosphate,** which occurs as a native mineral and which also forms the mass of the mineral constituents of the bones of animals. The small amount of phosphorus present in the soil is collected by the growing plants ; the herbivorous animals in their turn consume the phosphorus which has been accumulated by the plants, and from the bones of animals chemists and manufacturers derive the phosphorus of which they stand in need.

143. **Phosphorus,** when perfectly pure, is a transparent, colorless, wax-like solid of 1.8 specific gravity, which, when freshly cut, emits an odor like garlic, though under ordinary conditions this odor is overpowered by the odor of **ozone,** which, as has been previously stated (§ **103**), is developed when phosphorus is exposed to the air. It unites with oxygen

readily, even at the ordinary temperature of the air, and with great energy at somewhat higher temperatures (above 60°); when in contact with air, it is all the while undergoing slow combustion.

If the temperature of the slowly-burning phosphorus be slightly increased in any way, the mass will burst into flame and be rapidly consumed. On account of this extreme **inflammability**, phosphorus must always be kept under water: it is best also to cut it under water, lest it become heated to the kindling-point by the warmth of the hand, or by friction against the knife; for, when once on fire, it is exceedingly difficult to extinguish it, and in case it happens to burn upon the flesh, painful wounds are inflicted, which are very difficult to heal.

On account of this easy inflammability by friction, **phosphorus** is extensively employed for making matches. The matter upon the end of an ordinary friction-match usually contains a little phosphorus, together with some substance capable of supplying oxygen, such as red-lead, black oxide of manganese, saltpetre or potassium chlorate. The phosphorus and the oxidizing agent are kneaded into a paste made of glue or gum, and the wooden match-sticks, the ends of which have previously been dipped in melted sulphur, are touched to the surface of the phosphorized paste, so that the sulphured points shall receive a coating of it. The sulphur serves merely as a kindling material, which, as it were, passes along the fire from the phosphorus to the wood. By rubbing the dried, coated point of the match against a rough surface, heat enough is developed to bring about chemical action between the phosphorus and the oxygen of the other ingredient, combustion ensues, the sulphur becomes hot enough to take on oxygen from the air, and finally the wood is involved in the play of chemical force.

Exp. 57. — Put a piece of phosphorus as big as a grain of wheat upon a piece of filter-paper, and sprinkle over it some lampblack, or powdered bone-black. The phosphorus will melt after a time and will finally take fire. As stated above, phosphorus when exposed to the air is all the time undergoing slow combustion; this action is attended by evolution of heat. Both the lampblack and the paper are bad conductors of heat, and serve to prevent the phosphorus

from losing that developed by the oxidation. Moreover, as will be explained more fully hereafter under carbon, the vapor of phosphorus which rises continually is absorbed by or dragged into the pores of the bone-black and brought into intimate contact with oxygen which is or has been absorbed from the air. Chemical action ensues between the phosphorus vapor and the oxygen gas, and as the heat which is generated is retained, the phosphorus ultimately takes fire.

144. At the ordinary temperature of the air, and still more at somewhat higher temperatures, phosphorus shines with a greenish-white light, as may be seen by placing the phosphorus in the dark; hence the name, **phosphorus,** from Greek words signifying light-bearing. This **phosphorescence** is seen when an ordinary friction-match is rubbed against any surface in a dark room.

145. In warm weather **phosphorus** is soft and somewhat flexible, and may then be bent without breaking. It melts at 44°, forming a viscid oily liquid, which boils at about 290° and is converted into colorless vapor. Phosphorus can readily be distilled in a retort filled with some inert gas, like hydrogen, nitrogen or carbonic acid. When heated to about 230°, out of contact with the air, phosphorus is converted into an **allotropic modification** known as **red phosphorus.**

Phosphorus is insoluble in water, but is somewhat soluble in ether, petroleum, benzol, oil of turpentine and other oils : it also dissolves abundantly in carbon bisulphide.

If a solution of phosphorus in carbon bisulphide be poured upon a sheet of filter-paper, the carbon bisulphide will soon evaporate, leaving the phosphorus in a very finely divided state. The phosphorus begins immediately to oxidize, and, as the paper is a bad conductor of heat, it presently will burst into flame. The paper, however, is not completely consumed, but a very considerable residue of carbon remains unburned. This depends upon the fact that the product of the combustion of the phosphorus, quickly covers the paper with a varnish which is not only incombustible in itself, but is quite impervious to air.

146. **Red Phosphorus.** — This remarkable **allotropic modification** of phosphorus is a body as unlike ordinary phosphorus

in most respects as could well be conceived. It is of a scarlet-red color, has neither odor nor taste, is not poisonous so far as is known, is not phosphorescent, does not take fire at ordinary temperatures, is insoluble in bisulphide of carbon, and in general behaves altogether differently from the ordinary modification. It is easy, however, to convert one variety into the other. If ordinary phosphorus be heated to 230° out of contact of the air, the red variety is formed : if this be heated still further to 260°, it changes back into the ordinary variety.

Exp. 58. — In a narrow glass tube, No. 6, about 30 c. m. long and closed at one end, place a quantity of red phosphorus as large as a small pea ; heat the phosphorus gently over the gas-lamp and note that a sublimate of a light-colored substance is quickly deposited upon the cold walls of the tube a short distance above the heated portion. This light-colored sublimate is ordinary phosphorus, as may be shown by cutting off the tube just below the sublimate, after the glass has been allowed to cool, and then scratching the coating with a piece of wire : the coating will take fire. The air in the narrow tube employed is deprived of its oxygen by the combustion of a small portion of the phosphorus at the moment of its transformation from the red to the ordinary condition : the remaining phosphorus is thus enveloped in nitrogen, and so protected from further loss.

Red phosphorus is employed, to a certain extent, as an adjunct to the so-called *safety-matches*. Such matches contain no phosphorus in themselves, and will not take fire readily by friction upon an ordinary rough surface, though they burst into flame at once when rubbed upon a surface specially prepared with red phosphorus. The matter upon the tips of safety-matches is usually a mixture of potassium chlorate and antimony sulphide, made into a paste by means of glue : the surface upon which the match is to be rubbed is composed of red phosphorus, black oxide of manganese and glue. In favor of the use of red phosphorus for matches are the facts, that, unlike ordinary phosphorus, it is not deleterious to the workmen who have to deal with it, and it is far less liable to be set on fire by accidental friction.

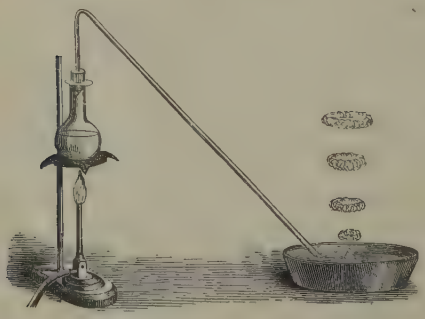
147. **Phosphorus** combines readily with many other elements besides oxygen. The ordinary modification of phosphorus combines violently with sulphur at temperatures near the melting-

point of sulphur, the act of combination being attended with vivid combustion and loud explosion. With chlorine, bromine and iodine, ordinary phosphorus unites directly at the ordinary temperature of the air, the combination being rapid and attended with inflammation. Phosphorus unites directly with most of the metals forming **phosphides.**

148. **Compounds of Phosphorus and Hydrogen.** — There are three compounds of phosphorus and hydrogen; of which, at ordinary temperatures, one is gaseous, H_3P, one liquid, H_2P, and one solid, HP_2. The gaseous compound, or rather the gaseous compound charged with the vapor of the liquid compound, is somewhat interesting, from the fact that it takes fire spontaneously, immediately on coming into contact with the air.

Exp. 59. — In a thin-bottomed flask of about 140 c. c. capacity, put 1 grm. of phosphorus and 115 c. c. of hydrate of sodium, obtained by dissolving 40 grms. of common caustic soda in 110 c. c. of water. Pour two or three drops of ether upon the liquid in the neck of the flask, then close the flask with a cork carrying a long delivery-tube of glass, No. 5. Place the flask over the gas-lamp, upon the wire-gauze ring of the iron stand, and immerse the end of the delivery-tube in the water-pan, then gently heat the flask. The ether is added to the contents of the flask, in order that the last traces of air may be expelled from the flask by the vapor which arises from this highly volatile liquid as soon as it is warmed.

Fig. 30.

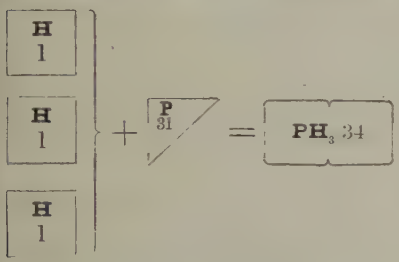


As the soda-solution becomes hot, small bubbles of gas will be seen to arise from the surface of the phosphorus, and in a short time large bubbles of gas will escape from the delivery-tube: each of these bubbles, as it comes in contact with the air at the surface of the water, will spontaneously burst into flame, and burn with a vivid light and

the formation of beautiful rings of white smoke, if the air be not disturbed by draughts. In burning, the **hydrogen phosphide** is converted into **phosphoric acid**, and of this product the white smoke is, of course, composed.

$$2\,H_3P + 8\,O = 2\,H_3PO_4.$$

The atomic weight of phosphorus is 31 ; the specific gravity of its vapor has been found to be 62.1. In this respect phosphorus differs from the elements already studied where the combining weights and the unit-volume weights have been identical ; it follows that, if the molecule of hydrogen contains two atoms of hydrogen, the molecule of phosphorus will contain four atoms of phosphorus (p. 91). If we compare the formula of hydrogen phosphide, H_3P (§ 148), with that of ammonia, H_3N, we have the atom of phosphorus, which weighs 31, combining with the same quantity of hydrogen by weight as the atom of nitrogen ; but while from two volumes of ammonia-gas we may set free three volumes of hydrogen and one volume of nitrogen, from two volumes of hydrogen phosphide we have three volumes of hydrogen and only half a volume of phosphorus vapor. The composition of hydrogen phosphide may thus be represented by the accompanying diagram.



149. **Oxides of Phosphorus.** — There are three **oxides of phosphorus** answering to the formulæ P_2O, P_2O_3, P_2O_5.

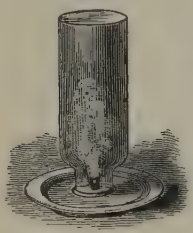
Hypophosphorous Anhydride (P_2O). — It is doubtful whether this oxide has been isolated. The corresponding acid, however, H_3PO_2 ($3\,H_2O$, $P_2O = 2\,H_3PO_2$), is known, as are also the corresponding salts, the **hypophosphites** of certain metals : the hypophosphite of barium, for instance, is $Ba\,H_4P_2O_4$.

Phosphorous Anhydride (P_2O_3) is formed by burning phosphorus with a limited supply of air. It is a white amorphous substance, very soluble in water, and burning in the air to phosphoric anhydride (P_2O_5). The corresponding acid is H_3PO_3 ($3\,H_2O$, P_2O_3) and the corresponding salts are called **phosphites**.

150. **Phosphoric Anhydride** (P_2O_5). — This oxide of phosphorus is the product of the rapid combustion of phosphorus in an excess of air or oxygen.

Exp. 60. — Dry thoroughly a large porcelain plate, a small porcelain capsule and a wide-mouthed bottle of two litres' capacity, by warming them at a fire ; place the capsule upon the plate and put in the capsule a bit of dry phosphorus, of the weight of about half a gramme ; light the phosphorus and cover it at once with the inverted bottle. The phosphoric anhydride, formed by the combustion of the phosphorus, will be deposited as a white powder, like flakes of snow, upon the sides of the bottle, and much of it will fall down upon the plate below.

Fig. 31.



The flocculent, amorphous, odorless powder, thus obtained, unites with water with remarkable facility : if it be left in the air for a few minutes, it deliquesces completely ; upon being thrown into water, it dissolves with a hissing noise and development of much heat. In order to preserve it, it must be placed in a dry tube, and the tube closed by sealing it in the lamp.

151. **Phosphoric Acid.** — By the union of **phosphoric anhydride** with **water,** there are formed three distinct acids : **meta-phosphoric acid** (HPO_3), **pyro-phosphoric acid** ($H_4P_2O_7$) and **ordinary** or **tribasic phosphoric acid** (H_3PO_4). Corresponding to these three varieties of phosphoric acid, there are three series of **phosphates,** the **meta-phosphates,** the **pyro-phosphates** and the **ordinary phosphates.**

The number of possible phosphates is much increased from the fact that while meta-phosphoric acid (HPO_3), like nitric acid, is **monobasic,** pyro-phosphoric acid ($H_4P_2O_7$) is **tetrabasic,** i.e., has four replaceable atoms of hydrogen, and the ordinary phosphoric acid (H_3PO_4) is **tribasic.** (See § 134.)

152. **Empirical and Rational Formulæ.** — It has already been stated that when phosphoric anhydride is thrown into water, it unites with a portion of the water to form phosphoric acid. The

reaction may be thus symbolized : $P_2O_5 + H_2O = H_2O, P_2O_5 = H_2P_2O_6 = 2\,HPO_3$ (meta-phosphoric acid). If the anhydride be thrown into hot water, the reaction is $P_2O_5 + 3\,H_2O = 3\,H_2O, P_2O_5 = H_6P_2O_8 = 2\,H_3PO_4$ (ordinary phosphoric acid). We may represent meta-phosphoric acid by the formula H_2O, P_2O_5 or by HPO_3 ; we may represent ordinary phosphoric acid by $3\,H_2O, P_2O_5$ or by H_3PO_4 : in these cases we have two formulæ to denote one and the same substance. If ordinary phosphoric acid were analyzed, it would be found to contain, for every three parts by weight of hydrogen, thirty-one parts of phosphorus and sixty-four (4×16) parts of oxygen. The result of the analysis would be expressed most simply by the formula H_3PO_4.

A formula which simply represents the number of atoms of each element in one molecule of any substance, as determined by analysis, is called an **empirical** formula. The truth of such a formula depends solely upon the correct performance of the analytical process, and upon the accuracy with which the atomic weights have been determined. Concerning such formulæ, there is little room for difference of opinion : they express all that we actually *know* of the elementary composition of any compound body. Chemists have, however, endeavored to contrive formulæ which should express something more than the mere elementary composition by weight ; which should recall the materials from which the formulated substance was made, and prophesy the products of its decomposition ; which should not only name and number the atoms of the substance, but should also suggest such a grouping or arrangement of those atoms as might serve to interpret its known reactions. Such formulæ are called **rational** formulæ. In the present case $3\,H_2O, P_2O_5$ is a rational formula of phosphoric acid. It recalls the fact that the acid can be made by causing phosphoric anhydride to unite with water.

It is not altogether a matter of indifference whether phosphoric acid be written $3\,H_2O, P_2O_5$ or H_3PO_4 ; for in one case the weight of the molecule would be 196 and in the other 98. If it were possible to obtain this compound in the state of vapor, and the vapor could be weighed, the weight of the molecule could be found (§ 139) by multiplying the vapor density by two. It is usual to regard the shorter formula as representing the molecule. The same difficulty occurs in the case of other compounds, nitric acid, for instance ; the molecule of nitric acid may be $H_2O, N_2O_5 = 126$ or $HNO_3 = 63$. In some

reactions it is more convenient to employ one formula, and in other reactions the other formula.

It is evident that there may be various **rational formulæ** for the same substance : in fact, for **acetic acid**, a compound of carbon, oxygen and hydrogen to be described in a subsequent chapter, no fewer than nineteen formulæ have been proposed.

153. All the acids (except those formed by the union of hydrogen with members of the chlorine group) and the corresponding salts may be written in a manner similar to that employed in the case of phosphoric acid $3\,H_2O, P_2O_5$: thus, — nitric acid, H_2O, N_2O_5 ; sodium nitrate, Na_2O, N_2O_5 ; potassium sulphate, K_2O, SO_3. Such formulæ are called **dualistic**, because they represent these bodies as of a dual nature, — as being made up of two oxides which were distinct before they were brought together to form the compound, and will be distinct when separately extracted from it : in a dualistic formula these two distinct parts are conventionally represented as having some separate existence within the compound itself. The supposition is not unnatural : thus, for example, common plaster of Paris is a substance containing the metal calcium and the elements sulphur and oxygen in the proportions by weight which are correctly expressed by the formula $CaSO_4$; but this substance may be made by methods which suggest another formula. If we put together quicklime, CaO, and sulphuric anhydride, SO_3, in due proportions, under suitable conditions, plaster of Paris, or, as its chemical name is, calcium sulphate, results : $CaO + SO_3 = CaO, SO_3$; or if we mix slaked lime, CaO, H_2O, with sulphuric acid, H_2O, SO_3, in proper proportions, at a suitable temperature, we shall again obtain calcium sulphate, and water will be eliminated : $CaO, H_2O + H_2O, SO_3 = CaO, SO_3 + 2\,H_2O$.

154. Another way of writing chemical formulæ is in accordance with the doctrine of **types**. According to this doctrine, every possible chemical combination may be imagined to be built upon the plan, or framed upon the type or model, of some one of three substances, chlorhydric acid (or free hydrogen), water and ammonia. These substances must be regarded as types only with reference to the supposed grouping of atoms in the compounds : the external properties of various substances referred to the same type may be totally different. Examples of compounds referred to the different types are : —

Type. Chlorhydric acid.	Free Hydrogen.	Sodium chloride.	Methyl hydride.
$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}H\\H\end{matrix}\right\}$	$\left.\begin{matrix}Na\\Cl\end{matrix}\right\}$	$\left.\begin{matrix}(CH_3)\\H\end{matrix}\right\}$
Type. Water.	Sodium hydrate.	Nitric acid.	Alcohol.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}Na\\H\end{matrix}\right\}O$	$\left.\begin{matrix}NO_2\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O$
Type. Ammonia.	Aniline.	Methylamine.	Acetamide.
$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}(C_6H_5)\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}(CH_3)\\H\\H\end{matrix}\right\}N$	$\left.\begin{matrix}(C_2H_3O)\\H\\H\end{matrix}\right\}N$

It will be noticed in these examples that the hydrogen of the type may be replaced, not only by a single element, but also by a group of elements. Such groups of elementary atoms are called **compound radicals**, and, like the elementary atoms themselves, differ in their replacing power, some being *univalent*, some *bivalent*, etc.

The **typical formula** of some substances is written by regarding the substance as built upon the type of the double molecule of the typical compound : other substances are regarded as built upon a *mixed* type. The following examples will serve to illustrate a few of these cases : —

Type.	Sulphuric acid.	Calcium sulphate.	Lead nitrate.
$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(SO_2)''\\H_2\end{matrix}\right\}O_2$	$\left.\begin{matrix}(SO_2)''\\Ca''\end{matrix}\right\}O_2$	$\left.\begin{matrix}2\,(NO_2)\\Pb''\end{matrix}\right\}O_2$
Type.	Urea.	Type.	Glycerin.
$\left.\begin{matrix}H_2\\H_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}(CO)''\\H_2\\H_2\end{matrix}\right\}N_2$	$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}(C_3H_5)'''\\H_3\end{matrix}\right\}O_3$
Type.	Sulphurous acid.		
$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\(SO_2)''\\H\end{matrix}\right\}O$		

It is often convenient to mark the fact that an elementary atom or a radical is bivalent or trivalent by the use of the proper number of accents placed at the right hand of the symbol, as has been done in these examples.

These typical formulæ will be found especially useful in the consid-

eration of the compounds of carbon ; it is, however, to be distinctly remembered that a rational formula is never to be regarded as the expression of an absolute truth, but only as a guide in classification, an aid to the memory and a help in instruction ; while the empirical formula expresses all that is actually known of the composition of any given body.

CHAPTER XIII.

ARSENIC, ANTIMONY AND BISMUTH.

ARSENIC (AS).

155. In small quantity **arsenic** is very widely distributed in nature. It is sometimes found free in the metallic state, but generally in combination with oxygen or sulphur and some one of the metals, such as iron, cobalt, nickel and copper.

156. **Arsenic** is a brittle solid of a steel-gray color and metallic lustre. At a dull red heat it may be converted into a vapor which has a peculiar garlic odor. Heated in the air or in oxygen, arsenic burns with a whitish flame producing the white **arsenic teroxide** (**arsenious anhydride**). Arsenic combines readily with chlorine, bromine, iodine and sulphur ; it also unites by fusion with most metals, forming alloys, which the arsenic tends to make hard or brittle. In the manufacture of shot, a little arsenic is added to the lead to facilitate the formation of regular globules.

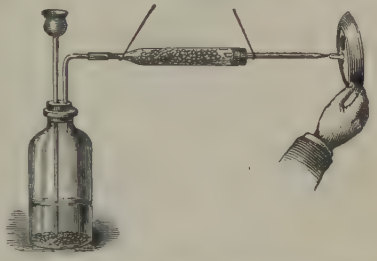
The symbol of **arsenic** is **As** ; its atomic weight is **75.** Like phosphorus, the specific gravity of its vapor is double its atomic weight, and consequently its molecular symbol is As_4.

157. **Hydrogen arsenide** or **arseniuretted hydrogen** (H_3As) is a colorless gas, having a fetid odor : even when very much diluted with air, it is intensely poisonous, and fatal results have repeatedly followed its accidental inhalation. The gas may be prepared in an impure state mixed with hydrogen by introducing a solution of some compound of arsenic into a

generator in which hydrogen is being produced from zinc and a dilute acid.

Hydrogen arsenide burns in the air with a whitish flame, forming water and a white smoke of **arsenious anhydride**; but if a cold body, like a piece of porcelain, for example, be introduced into a jet of the burning gas, the hydrogen alone will burn, and the arsenic will be deposited in the metallic state upon the porcelain surface, forming a lustrous black spot. This effect is precisely similar to the deposition of soot on a cold body held in the flame of a candle. The gas is also decomposed when caused to pass through tubes heated to dull redness, metallic arsenic being deposited as a brown or blackish mirror, while hydrogen gas escapes. These properties of hydrogen arsenide are made use of in testing for the presence of arsenic in cases of suspected poisoning.

Fig. 32.



158. **Compounds of Arsenic and Oxygen.** — There are two well-defined oxides of arsenic, — **arsenious anhydride** (As_2O_3) and **arsenic anhydride** (As_2O_5).

159. **Arsenious anhydride** (As_2O_3) often called *arsenious acid*, or *white arsenic*, is formed when metallic arsenic or arsenical ores are heated in the air. It ordinarily occurs in small octahedral crystals. When heated with free access of air, it volatilizes without change: if heated in contact with carbon, it gives up its oxygen, and metallic arsenic is liberated. Arsenious anhydride is somewhat soluble in water: it dissolves readily in hot chlorhydric acid; but, when the solution cools, most of the arsenious anhydride is deposited unchanged.

Exp. 61. — Place a few particles of "arsenious acid" * in an open

* The substances now designated as **anhydrides** were formerly called **acids** as stated in § 63. In the case of sulphurous, arsenious and carbonic anhydrides, the popular names sulphurous, arsenious and carbonic acids have such currency that they will be employed in this Manual where no ambiguity can arise from such use.

tube of hard glass (No. 5) about 10 c. m. long, and heat over the lamp, holding the tube in a sloping position : the white solid will be volatilized, but it will immediately be deposited again upon the cold part of the tube. By the aid of a lens, this deposit may be seen to be crystalline.

Fig. 33.

Exp. 62. — Drop into the point of a drawn-out tube of hard glass, No. 5, a morsel of arsenious acid, and above it place a splinter of charcoal (Fig. 33) ; heat the coal red-hot in the flame of the lamp, and then volatilize the arsenious acid. The acid will give its oxygen to the coal, and the arsenic will be deposited in a ring on the cold part of the tube, presenting a brilliant metallic appearance.

Exp. 63. — Throw a particle of arsenious acid upon a piece of red-hot charcoal : the acid will be partly reduced, and the peculiar garlic odor of the vapor of metallic arsenic will be perceived.

160. **Arsenious acid** is a violent poison, all the more dangerous, because it has neither taste nor odor to warn the victim of its presence : two decigrammes of it will cause death. All the soluble salts of arsenious acid are likewise horribly poisonous. The best antidote to the poison is a mixture of moist, freshly precipitated iron hydrate and caustic magnesia.

Arsenious acid is largely used in the manufacture of a brilliant green pigment, a compound of arsenite and acetate of copper commonly called Paris green ; it is applied as an oxidizing agent in the manufacture of glass ; it is consumed in considerable quantities for poisoning vermin, and for producing the arsenic acid which is used in the dyeing and printing of cloth ; it is used in very small doses as a remedy for asthma, and in some skin diseases.

161. **Arsenious anhydride** is soluble in water. The solution is slightly acid, but it is doubtful whether a definite compound of the anhydride with the elements of water is formed ; if so, it would be properly designated as **arsenious acid** : there are compounds of various metals (called **arsenites**) which would imply an arsenious acid of the formula H_3AsO_3. Thus **silver arsenite** is Ag_3AsO_3.

162. **Arsenic anhydride** (As_2O_5) is prepared by heating **arsenic acid** to dull redness. It forms a white amorphous mass, which by long exposure to water is gradually converted back into arsenic acid.

Arsenic acid (H_3AsO_4) is obtained by oxidizing **arsenious anhydride** with nitric acid, aqua regia or other oxidizing agents. The corresponding salts of the metals are called **arseniates.** Arsenic acid and some of the arseniates are used in dyeing.

163. **Sulphides of Arsenic.** — Two sulphides of arsenic occur native, one (As_2S_2) is called **realgar.** It is used in pyrotechny. The other (As_2S_3) is called **orpiment.** It is also prepared artificially, and is used somewhat as a pigment.

ANTIMONY (Sb).

164. **Antimony,** like arsenic, is found native : it also occurs alloyed with other metals, especially with arsenic, nickel and silver. There exist also a considerable number of minerals, which consist of, or contain, large proportions of the compounds of antimony with oxygen and sulphur. All the antimony of commerce is obtained from the mineral tersulphide, Sb_2S_3. The symbol for antimony is **Sb**, from the Latin name of the substance, *Stibium.*

165. **Antimony** is a brittle metal, having a bluish-white color, a brilliant lustre and a highly crystalline structure. The cakes of the commercial metal usually present upon their upper surfaces beautiful stellate or fern-like markings. Antimony melts at 450°, gives off vapors at a low red heat and takes fire at full redness, burning brilliantly with evolution of white fumes of the **teroxide** (Sb_2O_3). The atomic weight of antimony is 120.

Antimony enters into the composition of several very valuable alloys. *Type metal* is an alloy of lead and antimony, containing about 20 per cent of antimony. For stereotype plates $\frac{1}{8}$ to $\frac{1}{5}$ of tin is usually added to this alloy. The common white metallic alloys, such as *Britannia metal*, pewter, etc., used for cheap teapots, spoons, forks and like utensils, are variously compounded of brass, tin, lead, bismuth and an-

timony. The value of antimony in these alloys depends upon the hardness which it communicates to the compounds, without rendering them inconveniently brittle.

166. **Hydrogen antimonide** (H_3Sb ?) is a colorless, inodorous gas which resembles **hydrogen arsenide** in being decomposed by heat ; it burns in the air with a whitish flame and gives off a smoke of **antimony teroxide** : when a bit of cold porcelain is held against a burning jet of the gas, a sooty spot of metallic antimony is deposited on the porcelain. These spots of metallic antimony are distinguished from those of arsenic, obtained in a similar manner from **hydrogen arsenide** by difference in lustre, volatility and solubility in various chemical agents.

167. **Antimony and Oxygen.** — Antimony forms two well-defined oxides, — **antimony teroxide** (Sb_2O_3) and **antimonic anhydride** (Sb_2O_5). **Antimony teroxide** occurs as a native mineral, and is formed when metallic antimony is burned in the air. **Antimonic anhydride** is formed by heating **antimonic acid.** The acid may be obtained by oxidizing metallic antimony with nitric acid. A third oxide of antimony occurs native. Its formula is Sb_2O_4 and it may be regarded as a compound of the other two oxides, — Sb_2O_3, $Sb_2O_5 = 2\ Sb_2O_4$.

168. **Antimony and Chlorine.** — Powdered antimony takes fire when thrown into chlorine gas (**Exp. 32, § 81**) ; it also combines very energetically with bromine and iodine. When very finely powdered, it is dissolved by boiling chlorhydric acid, with evolution of hydrogen ; if a little nitric acid be added to the chlorhydric, the metal dissolves easily, to form a solution of **antimony terchloride** ($SbCl_3$).

Antimony terchloride at the ordinary temperature is a translucent yellowish substance of fatty consistency, whence its popular name, "butter of antimony." When thrown into water, it is decomposed into chlorhydric acid and antimony teroxide, which, however, remains united with a portion of the chloride, forming a white powder which contains antimony, chlorine and oxygen, but is somewhat variable in composition.

Fig. 34.

Exp. 64. — In a flask of about 200 c. c. capacity, heat gently 0.5 grm. of finely-powdered

antimony with 30 c. c. of strong chlorhydric acid, to which 10 drops of nitric acid have been added. When complete solution has been effected, pour a little of the chloride into water, to demonstrate the decomposition just referred to. Evaporate the rest of the solution to the consistency of a thick sirup : it is the butter of antimony.

169. **Antimony and Sulphur.** — The native mineral known as **gray antimony** or **antimony glance** is **antimony tersulphide** (Sb_2S_3). It is the source of the antimony of commerce.

BISMUTH (Bi).

170. The metal **bismuth** is found chiefly in the metallic state, but also occurs in combination with sulphur, oxygen and tellurium. It is prepared for the arts almost exclusively from **native bismuth.** It is a tolerably hard, brittle metal, of a grayish-white color with a reddish tinge. When pure, it crystallizes more readily than any other metal ; by the method of fusion (§ **113**) it may be obtained in most beautiful crystals, made highly iridescent by the thin film of oxide which forms on their surfaces while they are still hot.

Bismuth promotes the fusibility of metals with which it is alloyed to an extraordinary extent. The most remarkable alloy of bismuth is that known as "fusible metal." When composed of 1 part of lead, 1 part of tin and 2 parts of bismuth, this alloy melts at 93°.75. The symbol of bismuth is **Bi** ; its atomic weight is 210.

171. There is no compound of bismuth and hydrogen as yet known. There are three oxides corresponding to the oxides of antimony, — bismuth teroxide (Bi_2O_3), bismuthic anhydride (Bi_2O_5) and the oxide Bi_2O_4 which may be regarded as a compound of the other two. Bismuth terchloride ($BiCl_3$) resembles antimony terchloride. It is decomposed by water into chlorhydric acid, which dissolves a portion of the chloride, and a precipitate containing bismuth, chlorine and oxygen, and called *bismuth oxychloride* (**BiOCl**).

172. **The Nitrogen Group of Elements.** — The five elements, nitrogen, phosphorus, arsenic, antimony and bismuth, form a well-marked natural group of elements. In the first place, the elements themselves exhibit a definite gradation of properties,

and, secondly, the analogy in composition and properties manifested by the similar compounds of the five elements is most striking and complete.

Nitrogen is a gas, phosphorus a solid whose specific gravity varies from 1.8 to 2.2, arsenic has the specific gravity of 5.6, antimony of 6.7, while that of bismuth rises to 9.8. The metallic character is most decided in bismuth, is somewhat less marked in antimony, is doubtful in arsenic and almost vanishes in phosphorus. The series of corresponding hydrides, oxides, chlorides and sulphides, which the elements of this group form, are very perfect: they prove the general chemical likeness of the five elements: —

Hydrides.	*Oxides.*	*Oxides.*	*Oxides.*	*Chlorides.*	*Sulphides.*
NH_3	N_2O_3	N_2O_4	N_2O_5	NCl_3(?)	P_2S_3
PH_3	P_2O_3	Sb_2O_4	P_2O_5	PCl_3	As_2S_3
AsH_3	As_2O_3	Bi_2O_4	As_2O_5	$AsCl_3$	Sb_2S_3
SbH_3	Sb_2O_3		Sb_2O_5	$SbCl_3$	Bi_2S_3
	Bi_2O_3		Bi_2O_5	$BiCl_3$	
					P_2S_5
				PCl_5	As_2S_5
				$SbCl_5$	Sb_2S_5

When the qualities of the corresponding compounds which the members of the nitrogen group form with other elements are duly taken into account, it will be apparent that the relative chemical power of each element of the group may be inferred from its position in the series of elements: —

$$\mathbf{N} = 14,\ \mathbf{P} = 31,\ \mathbf{As} = 75,\ \mathbf{Sb} = 122,\ \mathbf{Bi} = 210.$$

The chemical energy of these five elements, broadly considered, follows the opposite order of their atomic weights.

CHAPTER XIV.

CARBON (C).

173. **Carbon** is an extremely important and a very abundant element. All organic substances, all things which have life, contain it. In the mineral kingdom, the various forms of coal, graphite, petroleum, asphaltum, and all the different varieties of limestone, chalk and marble, contain it in large proportion. It is found also in the atmosphere and in the waters of the globe, and though existing therein in comparatively small proportion, it is an ingredient not less essential than either of their other constituents for the maintenance of the actual balance of organic nature. All vegetable life is directly dependent upon the presence of the compound of carbon (**carbonic acid**) which exists in the atmosphere.

174. Three distinct **allotropic modifications** of carbon are distinguished, namely, 1. The **diamond**; 2. **Plumbago** or **graphite**; and 3. Ordinary **charcoal** or **lamp-black**; of this last modification there are many sub-varieties. In each of its modifications, carbon is an infusible, non-volatile solid devoid of taste and smell. While the several modifications differ among themselves in color, hardness, lustre, specific gravity, behavior towards chemical agents, power of conducting heat and electricity and in various other respects, they all agree in this, that, on being strongly heated in presence of oxygen, they unite with it and form the same compound, an oxide of carbon (CO_2).

175. **Diamond.** — The diamond is pure or nearly pure carbon and occurs in nature in octahedral crystals. Its rarity and its high refractive power as regards light, together with the difficulty with which it is worked, make it the most precious of gems. It is the hardest known substance. The diamond has not as yet been produced artificially.

The diamond is not attacked by the strongest acids or alka-

lies, not even by fluorhydric acid; nor is it acted upon by any of the non-metallic elements, with the exception of oxygen at high temperatures. At the ordinary temperature of the air, diamond undergoes no appreciable change. Out of contact with the air, or in an atmosphere which has no chemical action upon it, it suffers no alteration at the highest furnace heat; heated white-hot between the charcoal points of a powerful galvanic battery, it softens and swells up, forming a black brittle mass like coke; heated in oxygen gas, it burns to **carbonic acid** (CO_2).

176. **Graphite** or **Plumbago,** sometimes called "black-lead," is familiarly known as the material of common "lead pencils." It is found as a mineral in nature in various localities. It occurs both in the form of crystals and in the amorphous, massive state. In both forms it is always opaque, of a black or lead-gray color and metallic lustre.

Graphite is very friable; when rubbed upon paper, it leaves a black shining mark, whence its use for pencils. Amorphous graphite is so soft and unctuous to the touch that it is often used as a lubricant for diminishing the friction of machinery: but in spite of this seeming softness, the particles of which the masses of graphite are composed are extremely hard; they rapidly wear out the saws employed to cut these masses. In the air, at ordinary temperatures, graphite undergoes no change; hence its use for covering iron articles to prevent their rusting. By virtue of its greasy, adhesive quality, it is easy to cover iron with a thin, lustrous layer or varnish of it; the common stove-polishes, for example, are composed of powdered graphite.

177. **Gas-Carbon.** — An interesting sub-variety of carbon somewhat similar to graphite, and standing, as it were, between it and the ordinary modification of carbon, is obtained from the retorts in which common illuminating gas is manufactured. It is known as "**gas-carbon,**" or "carbon of the gas-retorts," and results from the burning on of drops of tar upon the interior walls of the retort, and the long-continued heating of the crust thus formed.

Gas-carbon is very hard, compact and dense: it has a metallic lustre, and conducts electricity like a metal. On account of its high conducting power, it is employed in the manufacture of galvanic batteries and of pencils for the electric lamp.

178. **Coke** and **Anthracite Coal** are impure sub-varieties of carbon which, from the chemical point of view, may be classed either with **graphite** or **charcoal**, or better between the two. They are less like graphite, however, than gas-carbon is. **Coke** is the residue resulting from the destructive distillation of soft or bituminous coal.

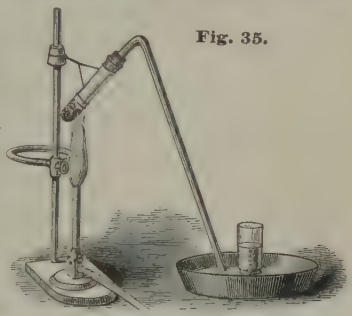


Fig. 35.

Exp. 65. — Put into a tube of hard glass, No. 1, 12 or 15 c. m. in length, enough bituminous coal, in coarse powder, to fill one-third of the tube. Fit to this ignition-tube a large delivery-tube of glass, No. 4, and support the apparatus upon the iron stand, as shown in the figure. Heat the coal in the ignition-tube, and collect in bottles the gas which will be evolved. The gas will burn with a yellow flame on the application of a match. This gas is, in the main, a mixture of several compounds of carbon and hydrogen; for the present, it may be regarded as carburetted hydrogen. It is, in fact, ordinary illuminating gas.

As soon as gas ceases to be given off from the coal, take the end of the delivery-tube out of the water, and when the ignition-tube has become cold, break it, and examine the coke which it contains. The coke used for domestic purposes is obtained as an incidental product in the manufacture of illuminating gas.

Bituminous coal is a substance of vegetable orgin, which appears to have been formed from plants by a process of slow decay going on without access of air and under the influence of heat, moisture and great pressure. Like vegetable matter in general, it is composed of carbon and hydrogen, together with small proportions of oxygen and nitrogen, and a certain quantity of earthy and saline substances, commonly spoken of as inorganic matter. On being heated in the air, it burns away almost completely after a while, leaving nothing but the inorganic components as ashes. But when heated

out of contact with the air, that is to say, when subjected to destructive distillation, as in Exp. 65, the volatile hydrogen is all driven off in combination with some carbon, either as gas or as a tarry liquid, and the residue, or **coke**, contains only carbon contaminated with the inorganic matters originally present in the coal.

In Europe, where anthracite is lacking, immense quantities of coke are prepared for metallurgical uses, the gas resulting from the decomposition of the coal being usually thrown away.

Anthracite is supposed to have been formed, like bituminous coal, from the slow decay of vegetable matter, and then to have been subjected to some sort of natural distillation by which it has been deprived of nearly all the hydrogen, nitrogen and oxygen of the original wood. It is thus a **coke** formed by natural agencies.

179. Both **coke** and **anthracite** are hard and lustrous. As compared with charcoal, they are rather difficult of combustion. Both anthracite and coke, the latter in spite of its porosity, conduct heat readily, as compared with charcoal; hence one reason of the difficulty of kindling them. In building a charcoal fire, the heat evolved by the combustion of the kindling material is almost all retained by the portions of charcoal immediately in contact with the kindling agent, but in the case of coke or anthracite, a large proportion of this heat is conducted off and diffused throughout the heap of fuel, so that no portion of the fuel can at once become very hot.

180. **Charcoal** or **Lamp-black** is commonly taken as the representative of the third or **amorphous** modification of carbon. This kind of carbon can be obtained in a state of tolerable purity, either by heating in a close vessel sugar, starch or some other organic substance which contains no inorganic constituents, or by burning oil of turpentine in a quantity of air insufficient for its complete combustion.

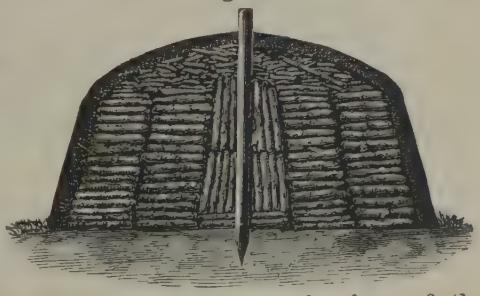
Charcoal can be obtained also by distilling wood in retorts in the same way that we have seen that coke can be procured from bituminous coal. (See **Exp. 65.**)

Exp. 66. — Provide an ignition-tube and a delivery-tube similar to those employed in Exp. 65. Fill the ignition-tube with shavings or small fragments of wood, arrange the apparatus as before and light

the gas-lamp. Collect in bottles the gas which is given off from the wood and test it as to its inflammability by applying a lighted match. After the flow of gas has ceased, remove the end of the delivery-tube from the water, plug it so that no air can enter the ignition-tube and lay the apparatus aside until it has become cold. Finally, remove the cork from the ignition-tube and take out the charcoal which is contained in it. Heat a portion of this charcoal upon platinum foil and observe the manner in which it burns : it will illustrate the fact that solid substances which are incapable of evolving volatile or gaseous matter do not burn with flame, — they merely glow.

For use in the arts charcoal is sometimes prepared by distilling the wood in retorts, but more generally by burning the wood with little access of air. Logs of wood are piled up into a large mound or stack around a central aperture, which subsequently serves as a temporary chimney and also for the introduction of burning substances for firing the heap. The finished heap is covered with chips, leaves, sods and a mixture of moistened earth and charcoal dust, a number of apertures being left open around the bottom of the heap for the admission of air and the escape of the products of distillation and combustion. The heap is kindled at the centre and burns during several weeks. When the process is judged to be complete, all the openings are carefully stopped in order to suffocate the fire, and the heap is then left to itself until cold. The charcoal retains the form of the wood, — the shape of the knots and the annual rings of the wood being still perceptible in it, — but it occupies a much smaller volume than the wood : generally its bulk does not amount to more than three-fourths of that of the wood, and

Fig. 36.



its weight never exceeds one-fourth the weight of the wood. Sometimes kilns built of brick are used instead of the rude heaps here described.

Where charcoal is prepared by distilling wood in retorts, the liquid products of distillation, namely, **tar** and **acetic acid** ("pyroligneous acid"), are saved and utilized.

181. **Lamp-black.** — Upon the large scale, **lamp-black** is manufactured by heating organic matters, such as tar, resin or pine knots, which contain volatile ingredients very rich in carbon, until vapors are disengaged, and then burning these vapors in a current of air insufficient for their complete combustion. The vapors consist of compounds of carbon and hydrogen, and the supply of air being insufficient to consume both hydrogen and carbon, a large portion of the carbon of the combustible does not burn, but is deposited as a very fine powder precisely similar to that which constitutes the black portion of common smoke. Lamp-black finds important applications in the arts as a pigment and as the chief ingredient of printers' ink.

Exp. 67. — Fill an ordinary spirit-lamp (Appendix, § 5) with oil of turpentine, light the wick and place over it an inverted wide-mouthed bottle of the capacity of a litre or more, one edge of the mouth of the bottle being propped up on a small block of wood, so that some air may enter the bottle. As the supply of air is insufficient for the perfect combustion of the oil of turpentine, a quantity of lamp-black will separate and be deposited upon the sides of the bottle.

Hydrogen kindles at a lower temperature than carbon, hence if the flame of a burning compound of carbon and hydrogen be cooled down below the temperature at which carbon takes fire, lamp-black will be formed, even if there be present an abundant supply of air.

Exp. 68. — Press down upon the flame of an oil-lamp or candle an iron spoon or a porcelain plate in such manner that the flame shall be almost, but not quite extinguished. The solid body not only ob-

structs the draught of air, and thereby interferes with the act of combustion, but it also cools the flame by actually conducting away part of its heat; the temperature is thus reduced to below the kindling-point of carbon, and a quantity of lamp-black remains unconsumed and adhering to the spoon or plate. The deposit of lamp-black is, of course, comparable with the spots of arsenic and antimony, alluded to in §§ 157, 166, as being obtained upon porcelain, as products of the incomplete combustion of the hydrogen compounds of these elements.

Fig. 37.

182. In all its varieties, **charcoal** is a very important chemical agent, chiefly because of the readiness and energy with which it combines with oxygen at high temperatures. It might almost be said that the art of **metallurgy,** as it now exists, is based upon the affinity of **carbon** for **oxygen.**

Exp. 69. — Mix two and a half grammes of copper oxide with a quarter of a gramme of powdered charcoal; place a portion of the mixture in an ignition-tube made of No. 3 glass, and heat it strongly in the gas-lamp. The charcoal will unite with the oxygen of the copper oxide, and the compound thus formed will escape in the form of gas, while metallic copper will remain in the tube.

This experiment is analogous to Exp. 62, where arsenious acid was reduced by means of charcoal. Both experiments are typical of the manner in which hot charcoal acts upon metallic oxides. At a white heat it removes oxygen from its combinations with some elements which hold it with great force, such as the oxides of sodium and potassium, phosphoric acid and water. If a current of steam be passed over red-hot charcoal, the steam is decomposed; the hydrogen is set free, and the oxygen of the steam combines with a portion of the carbon to form **carbon protoxide** (**CO**), an inflammable gas. The reaction which occurs may be formulated as follows: $\mathbf{C + H_2O = CO + 2\,H}$.

The **deoxidizing** power of charcoal, thus illustrated, is exhibited only at high temperatures. At the ordinary temperature of the air, the chemical energy of charcoal is exceed-

ingly feeble. Charcoal is, in fact, one of the most durable of substances. Specimens of it have been found at Pompeii and upon Egyptian mummies, to all appearance as fresh as if just prepared: the action of the air continued through centuries has exerted no appreciable influence upon it. Fence-posts which are sunk for a certain distance into the ground are often charred on the outside, and thus rendered more durable.

183. A physical property of **charcoal**, which is of great practical importance, is its power of **absorbing** and **condensing** within its pores a great variety of gases and vapors. Freshly-burned charcoal exposed to damp air, in a cellar for instance, will gain 10 or 12 per cent in weight in the course of a single day.

Exp. 70. — Take from the fire a piece of charcoal which has been heated to full redness for some time; thrust it under water so that it may be suddenly cooled, and observe that it sinks in the water and that few or no bubbles of gas escape from its pores.

Take another piece of charcoal which has long been exposed to the air and has not recently been heated, attach to it a quantity of sheet-lead sufficient to sink it in water, and immerse the whole in a large beaker-glass two-thirds full of hot water. The mobile water will immediately enter the pores of the charcoal, and a portion of the air which had previously been absorbed by these pores will be driven out, and can be seen escaping in bubbles through the water, chiefly from the broken ends of the coal.

To the presence of air and aqueous vapor, which has been thus absorbed, is to be attributed the snapping and crackling of old charcoal when it is thrown upon a hot fire.

Different gases are absorbed by charcoal in very different proportions: thus a cubic centimetre of dry, compact charcoal, such as that from boxwood, will absorb as much as 90 c. c. of ammonia-gas in the course of 24 hours; while in the same time it will absorb only 35 c. c. of carbonic acid and only 2 c. c. of hydrogen.

184. **Charcoal** is much employed as a **disinfecting agent.** It is capable of removing many offensive odors from the air,

such, for example, as the fetid products given off during the putrefaction of animal and vegetable substances. Animal matter in an advanced stage of putrefaction loses all offensive odor when covered with a layer of charcoal, and the flesh of a dead animal buried beneath a thin layer of charcoal will gradually waste away and be consumed without exhaling any unpleasant smell.

Exp. 71. — Place a small quantity of powdered charcoal in a bottle containing hydrogen sulphide gas, and shake the bottle. The odor of the hydrogen sulphide will quickly disappear. In the same way, an aqueous solution of hydrogen sulphide (Exp. 48) can be deodorized by filtering it through a layer of charcoal.

In all these cases, the use of charcoal as a **disinfectant** depends not merely upon its mechanical ability to absorb offensive gases, but also and mainly upon the fact that the absorbed gases are chemically destroyed within the pores of the coal by the oxygen which is sucked into these spaces from the air. The purifying action depends upon **oxidation**, upon the burning up of the offensive gases. The charcoal is in no sense an **antiseptic** or preservative agent proper to prevent decay ; on the contrary, it actually hastens the destruction of putrescible organic matters. Under ordinary circumstances, the pores of charcoal contain more or less oxygen which has been absorbed from the air, and any new gas which is dragged in is forced into intimate contact with this oxygen. If the new gas is one on which oxygen can act, it is destroyed ; and as fresh portions of the gas are absorbed by the charcoal, additional quantities of oxygen are also absorbed, so that the action may go on for a long time. A great merit of charcoal as a disinfectant is, that it constantly draws in to destruction the offensive matters around it; pans of charcoal placed about a room, — the wards of a hospital, for example, — the air of which is offensive, soon remove the unpleasant smell.

185. **Charcoal** not only destroys odors, but it removes colors as well, and for this purpose it has long been employed in the purification of sugar and of many chemical and pharmaceutical preparations. Almost any coloring matter can be removed from a solution by filtering the liquid through a layer of charcoal.

Exp. 72. — Provide four small bottles of the capacity of 100 or 200 c. c., and place in each of them a table-spoonful of bone-black (§ 186); into the first bottle pour a quantity of the blue compound of iodine and starch obtained in Exp. 39; into the second, a decoction of cochineal; into the third, a dilute solution of soluble indigo blue; into the fourth a solution of blue litmus, of logwood, or indeed of almost any other vegetable coloring matter; enough of the solution being taken in each instance to nearly fill the bottle. Cork the bottles and shake them violently, then pour the contents of each upon a filter (see Appendix, § 15), and observe that the filtrate is in each instance colorless, or nearly so. In case the first portions of the filtrate happen to come through colored, they may be poured back upon the filter and allowed to again pass through the coal.

Fig. 38.

In the purification of brown sugar, the coloring matters are removed in a manner similar to the foregoing, the colored sirup being filtered through layers of bone-black. Besides coloring matters, charcoal can absorb many other substances: sulphate of quinine, for example, is removed from its solutions, to a very considerable extent, by charcoal, and the same remark applies, with perhaps still more force, to strychnine. The bitter principle of the hop, "lupulin," may be entirely removed from ale by filtering the latter through bone-black.

In all these cases where coloring matters, and the like, are removed from solutions, the action of the coal appears to depend in the main directly upon the physical property of **adhesion**; the subsequent **oxidizing** action being here far less clearly marked than in the instances previously studied (§ 184) where gases are acted upon. Much of the absorbed color or other matter will usually be found attached to the surfaces of the coal, undecomposed and unaltered.

186. As obtained from different sources, charcoal exhibits very different degrees of **decolorizing** power; but of the varie-

ties commonly met with and to be procured in commerce, **bone-black** is the most efficient. **Bone-black** is prepared for the use of sugar-refiners, by subjecting bones to destructive distillation in large iron cylinders and carefully cooling the charcoal out of contact with the air. As dry bones contain about 66 per cent of mineral matter, the charcoal thus obtained is left in an exceedingly porous condition, distributed over and among the particles of the mineral matter.

187. **Compounds of Carbon and Oxygen.** — There are two of these compounds, — **Carbonic anhydride** (CO_2) and **carbon protoxide** (CO).

188. **Carbonic anhydride,** commonly called **carbonic acid** (CO_2), is always formed when carbon or any of its compounds is burned in an excess of air or of oxygen gas, or in contact with substances, gaseous, liquid or solid, which are rich in oxygen, and yield it readily to other bodies.

Exp. 73. — Place a live coal (charcoal) upon a deflagrating spoon, and thrust it into a bottle full of air, or, better, oxygen gas : when the coal has ceased to glow, pour into the bottle some lime-water, — a solution of common slaked lime in water, — and shake the bottle. The liquid will become milky and turbid, and, when left at rest, will deposit a white powder (calcium carbonate). The presence of carbonic acid can readily be detected by means of lime-water, since this insoluble precipitate of calcium carbonate is formed when the two substances are brought together.

From the formulæ of the class of bodies known as **carbonates** (sodium carbonate = Na_2CO_3), we should infer the existence of a **carbonic acid** of the formula H_2CO_3. Carbonic anhydride does dissolve in water, and the solution has a slightly acid reaction : it is, however, doubtful if a definite compound is formed. The term carbonic acid has, however, been so long applied to the oxide of carbon, CO_2, and the term has such a foothold in our language and literature, that it will be used in this chapter in its popular sense.

Exp 74. — As was just now said, carbonic acid may be produced also by heating carbon in contact with solid bodies which contain oxygen, such, for example, as the red oxide of mercury. Mix 11 grms. of red oxide of mercury with 0.33 grm. of charcoal ; place the

mixture in an ignition-tube arranged as in Figure 35 ; heat the tube and collect over water the gas which is evolved. Test the product with lime-water, as in Exp. 73. The reaction between the charcoal and the mercury oxide may be written as follows : —

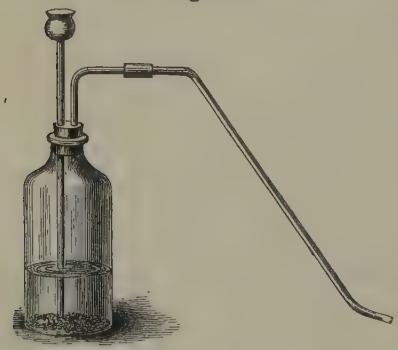
$$2\,HgO + C = CO_2 + 2\,Hg.$$

The metallic mercury set free condenses in droplets upon the cold upper portions of the ignition-tube. Here, again, as in Exps. 62 and 69, the metallic oxide is reduced by the charcoal.

189. **Carbonic acid** may readily be obtained from certain compounds called **carbonates,** several of which are abundant minerals. Common chalk, marble and limestone, for example, are composed of **calcium carbonate;** and carbonic acid can readily be obtained by strongly heating them, or by subjecting them to the action of strong acids.

Exp. 75. — In a gas-bottle of 500 or 600 c. c. capacity, arranged precisely as for generating hydrogen (see Exp. 11, § 35), place 10 or 12 grms. of chalk or marble in small lumps ; cover the chalk with water, and pour in through the thistle-tube concentrated chlorhydric acid, by small portions, in such quantity as shall insure a continuous and equable evolution of gas. Collect several bottles of the gas over water, then replace the anterior portion of the delivery-tube with a straight tube and collect one or two bottles of the gas by displacement ; carbonic acid gas is half as heavy again as air. The reaction between the calcium carbonate and the chlorhydric acid may be thus formulated : $CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2$.

Fig. 39.



190. At the ordinary atmospheric temperature and pressure, **carbonic acid** is a transparent, colorless gas, of a slightly acid smell and taste. It is **incombustible,** being already the product of the complete combustion of carbon, and is, moreover, inca-

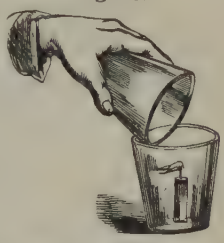
pable of supporting the combustion of most other bodies: it is also incapable of supporting animal life.

Exp. 76. — Thrust into a bottle of the gas, obtained in Exp. 75, a lighted candle, or, better, a large flame of alcohol burning upon a tuft of cotton; in either case the flame will be instantly extinguished.

191. The specific gravity of **carbonic acid** is 22; being thus 1.53 times heavier than air, it can be poured from one vessel to another almost as readily as if it were water.

Exp. 77. — From a large bottle or other vessel full of the gas, pour a quantity of carbonic acid upon the flame of a lamp or candle; that is to say, hold the mouth of the open bottle of carbonic acid obliquely over the candle flame, so that the gas shall fall like water upon it: the flame will immediately be extinguished.

Fig. 40.



Carbonic acid can be obtained in the liquid state by subjecting the gas to pressure. It can also be obtained in a solid snow-like state by exposing the liquid to cold.

192. **Carbonic acid gas** is soluble in water to a considerable extent. One measure of water at the ordinary temperature and pressure, will dissolve one measure of carbonic acid gas, but its solubility increases if the pressure be increased.

Exp. 78. — Into a long-necked flask or phial filled with carbonic acid, pour a quantity of water, close the bottle with the finger and shake it; immerse the mouth of the bottle in water, and remove the finger; water will rush into the bottle to supply the place of the gas which has been dissolved. Again place the finger upon the mouth of the bottle, shake the bottle as before and subsequently open it beneath the surface of the water; a fresh portion of water will flow into the bottle to supply the new vacuum; in this way, by repeated agitation with water, all of the carbonic acid in the bottle can be absorbed.

When subjected to increased pressure, carbonic acid gas dissolves in water much more abundantly than at the ordinary pressure of the air. Water thus surcharged with carbonic acid has an agreeable, acid, pungent taste, and effervesces briskly

when the compression is suddenly removed, as when the liquid is allowed to flow out into the air; such carbonic acid water flows from the earth in many localities as at Selters or Seltz in Germany (Seltzer water) and at Saratoga, N. Y. It is also prepared artificially, in large quantities, and sold as a beverage under the meaningless name of *soda-water*. The effervescent qualities of fermented liquors, such as cider, champagne and beer, are, in like manner, dependent upon the presence of compressed carbonic acid gas.

193. **Carbonic acid** is produced, not only in the actual combustion of all substances which contain carbon, but also during the **decay** and **putrefaction** of all animal and vegetable substances. During **fermentation** it is evolved in large quantities, and it is continually given off during the **respiration** of animals.

Exp. 79. — Dissolve 10 grms. of honey or molasses in 100 c. c. of water; fill a large test-tube with the mixture and add to it a few drops of bakers' or brewers' yeast; close the open mouth of the test-tube with the thumb, and invert it in a small saucer or porcelain capsule filled with the diluted sirup. Place the saucer and tube, with their contents, in a warm place, having a temperature of about 20° or 30°, and leave them there during 24 hours. In a short time fermentation sets in, and the sugar of the sirup is gradually converted into alcohol and carbonic acid.

$$\underset{\text{Sugar.}}{C_6H_{12}O_6} = \underset{\text{Alcohol.}}{2\,C_2H_6O} + 2\,CO_2.$$

The carbonic acid thus formed rises in minute bubbles, causing a gentle effervescence in the liquid, and collects in the upper part of the tube, while the alcohol remains dissolved in the liquid.

Exp. 80. — Provide two test-glasses or small bottles; place in each 15 or 20 c. c. of lime-water; through a glass tube, blow into the lime-water of one of the bottles air coming from the lungs. By means of bellows, to the nozzle of which a gas-delivery tube has been attached, force through the lime-water of the second bottle a quantity of fresh air. The clear liquid of the first bottle will quickly become turbid through deposition of calcium carbonate, while the lime-water of the second bottle will remain clear for a long while.

194. **Carbonic acid** is an exceedingly weak acid; it fails to

neutralize (§ 61) completely the causticity of hydrates, such as those of the alkaline metals ; the normal carbonate of sodium, for example, is decidedly **alkaline** in its reaction and properties. Almost all the carbonates are readily decomposed by acids, — even by very weak acids, — with an effervescence caused by the escape of carbonic acid : many, among them calcium carbonate, are decomposed by heat.

Carbonic acid is bibasic (§ 134) like sulphuric acid ; thus there exist a sodium carbonate, Na_2CO_3, and a hydrogen sodium carbonate, $HNaCO_3$ ("bicarbonate of soda").

195. **Carbon Protoxide** (CO), called also **carbonic oxide,** may be prepared by passing carbonic acid over hot charcoal ($C + CO_2 = 2\ CO$) or by heating the oxides of almost any of the metals with an excess of charcoal. The gas is, however, contaminated with some carbonic acid. It may be prepared pure as follows : —

Exp. 81.—In a flask of about 250 c. c. capacity, provided with a delivery-tube and with a safety-tube (Fig. 41), heat gently a mixture of 5 grms. of finely-powdered potassium ferrocyanide (yellow prussiate of potash) and 40 or 50 grms. of strong sulphuric acid. Collect the gas over water and test it as to its inflammability. Thrust also a lighted splinter into the gas and observe that it will be extinguished. The reactions which occur between the chemicals employed will be explained in a subsequent section (see § 387).

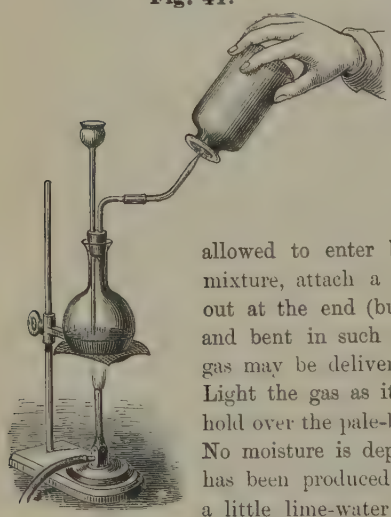
196. **Carbon protoxide** is a transparent, colorless gas, having little, if any, odor ; it may be liquefied, but with great difficulty. The gas is somewhat lighter than air, its specific gravity being 14, while that of air is 14.5. It is but little soluble in water, and may be collected over water without much loss. It extinguishes combustion just as hydrogen does, and destroys animal life. Unlike hydrogen and nitrogen, however, it is a **true poison.** It destroys life, not negatively by mere suffocation or exclusion of oxygen, but by direct noxious action. It is the presence of this gas which occasions the peculiar sensation of oppression and headache which is experienced in rooms into which the products of combustion have escaped from fires of charcoal or anthracite. Carbon protoxide is very much more

poisonous than carbonic acid. Much of the ill repute which attaches to carbonic acid really belongs to carbon protoxide, for since both these gases are produced by burning charcoal, many persons are liable to confound them; but carbonic acid is, comparatively speaking, almost innocuous.

197. **Carbon protoxide** plays a very important part in many metallurgical operations on account of the power which it possesses at high temperatures of taking away oxygen from many compounds containing that element. Much of the reducing action which is, commonly speaking, attributed directly to carbon, is really effected in practice through the mediation of the protoxide.

198. **Carbon protoxide** burns readily in the air, the sole product of the burning being carbonic acid. The gas forms an explosive mixture with air or oxygen.

Fig. 41.



Exp. 82. — To the apparatus employed in Exp. 81, provided air has not been allowed to enter by the cooling down of the mixture, attach a piece of glass tubing drawn out at the end (but not to a very fine point) and bent in such a manner that a stream of gas may be delivered upwards from the point. Light the gas as it flows out of the tube, and hold over the pale-blue flame a clean, dry bottle. No moisture is deposited. That carbonic acid has been produced may be proved by pouring a little lime-water into the bottle and shaking it about in the gas therein contained.

199. **Combustion.** — Now that we have become acquainted with carbon, hydrogen and oxygen, and with some of the more important compounds formed by the union of these elements, the subject of **combustion** can be more fully discussed than has been possible hitherto. The materials employed as com-

bustibles are, as a general rule, compounds of carbon and hydrogen; there are some exceptions to this rule, as when the metal magnesium is burned for light, or the heating of a sulphuretted ore is effected by the combustion of its own sulphur.

200. In almost all cases **artificial light** results from the incandescence of particles of solid matter, or of dense vapors. When the heat, which is an invariable accompaniment of chemical combination, can play directly upon such solid or semi-solid particles with force enough to ignite them, an exhibition of light will accompany the chemical change. The hydrogen flame affords no light, or as good as none, because in it nothing but a highly attenuated gas is heated. But when a solid body, such as the platinum wire or the piece of lime of § **41**, is placed in this non-luminous hydrogen flame, intense light is radiated from the heated solid.

Exp. 83. — Sprinkle fine iron filings into the flame of an alcohol lamp, or into the non-luminous flame of the gas-lamp, and observe the light given off by the particles of metal as they become incandescent while passing through the flame. Or rub together two pieces of charcoal above a non-luminous flame, in such manner that charcoal powder shall fall into the flame.

201. In ordinary luminous flames, such as those of candles, lamps and illuminating gas, the ignited substance is **carbon,** or rather a vapor or fog of certain **carbon compounds** containing more or less hydrogen.

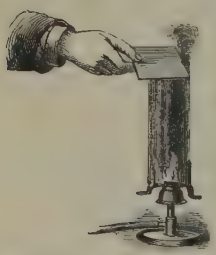
Ordinary illuminating gas may be decomposed by passing it through a tube heated red-hot; the carbon will separate, in a finely-divided state, while hydrogen will escape from the tube: or, by putting a cold body into a luminous gas-flame, the carbon is deposited as soot (see Exp. 68, § 181). This breaking up of the compounds of carbon and hydrogen under the influence of heat takes place when the gas is burned in the air, and if the supply of air furnished be insufficient to convert all the carbon and hydrogen to carbonic acid and water, the particles of carbon which escape unconsumed will cause the flame to be *smoky*. If the supply of air be excessive, the combustion will be complete, and no light will be afforded by the flame.

If we unscrew the tube of a common Bunsen lamp (Appendix, § 5) and light the gas as it issues from the slit (or holes) in the lower part of the burner, we shall have a luminous and perhaps even smoky flame. When, however, the tube is in its place, the gas becomes mixed with air which enters by the holes at the base of the lamp, and when the mixture is lighted, the gas is in intimate contact with air enough to burn it at once, and completely. A luminous flame may also be produced by simply closing the holes at the base of the lamp, with the fingers or by means of a metallic tube, as represented in Fig. 42.

Fig. 42.

If across the top of the chimney of a lighted Argand gas-burner, which is burning with a low flame, we slip a strip of sheet-iron, and thus obstruct the flow of air, the flame will increase in size, becoming more and more luminous, and finally will actually smoke. The amount of gas supplied has remained the same ; the difference in the amount of light is owing to the decrease of the supply of air. The murky flame, such as was obtained just before actual smoking began, in which the largest number of particles of carbon or heavy carbonaceous vapor are heated, although none of them are heated very hot, yields the largest amount of light that can be obtained from a given burner with a given sample of gas. Such a flame, however, does not furnish the light most agreeable to the eyes.

Fig. 43.



202. The flames of ordinary lamps and candles are, strictly speaking, **gas-flames.**

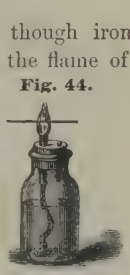
Exp. 84. — Construct a lamp as follows : To a wide-mouthed bottle of the capacity of about 50 c. c. fit a cork loosely ; bore a hole in the cork and place therein a short piece of glass-tubing, No. 3, open at both ends ; through this glass-tube draw a piece of lamp-wicking, or any loose twine, long enough to reach to the bottom of the bottle. It is essential, either that the cork should fit the bottle loosely, or that there should be a hole in the cork, in order that the

pressure of the external air may act upon the surface of the alcohol, — to this end a very small glass-tube may be inserted in the cork at some distance from the tube which carries the wick. Fill the bottle nearly full of alcohol, and, after a few minutes, touch a lighted match to the top of the wick. The fluid alcohol is drawn up out of the bottle by force of capillary attraction exercised by the pores of the vegetable fibre of which the wick is composed. When heat is applied to the alcohol at the top of the wick, some of it is converted into vapor; this vapor then takes fire, and, in burning, furnishes heat for the vaporization of new portions of the alcohol. From the top of the wick there is constantly arising a column of gas or vapor, and upon the exterior of this conical column chemical combination is all the while going on between its constituents and the oxygen of the air. The dark central portion of the alcohol flame is nothing but gas or vapor.

Exp. 85. — Thrust the phosphorus end of an ordinary friction-match directly into the middle of the flame of the alcohol-lamp of Exp. 84. The combustible matter upon the end of the match will not take fire in the atmosphere of carbonaceous gases, of which the centre of the flame consists; the wood of the match-stick, of course, takes fire at the point where it is in contact with the outer edge of the flame. The portion of the match in the centre of the flame becomes so strongly heated during its sojourn within the circle of fire, that it is ready to inflame as soon as it comes in contact with the air; it is therefore somewhat difficult to withdraw the match from the flame without its taking fire.

Exp. 86. — Hold a thin wire (best of platinum, though iron will answer well enough) or a splinter of wood across the flame of the alcohol-lamp, as shown in Fig. 44. The wire will be heated to redness, and the wood will burn, only at the outer edges of the flame where the gas and air meet; in the interior of the flame, the wire will remain dark and the wood unburned, for there is no combustion there, and comparatively little heat. If the wire be successively placed at different heights in the flame the size and shape of the internal cone of gas can easily be made out; it will appear, moreover, that the hottest part of the flame is just above the top of the interior cone of gas. As a rule, when glass-tubing, or the like, is to be heated in a flame, it should never be placed below this point of the greatest heat.

Fig. 44.



When a candle is lighted for the first time, the cotton of which the wick is composed takes fire, and is at once consumed for the most part, but, in burning, the cotton gives off considerable heat, and some of the wax or tallow of which the candle is composed is thereby melted and converted into oil. The liquid oil ascends the wick by virtue of capillary attraction, and is converted into vapor or gas by the heat of the cotton still burning at the stump of the wick ; this gas then burns precisely like the alcohol vapor in Exp. 84, and by the heat thus disengaged new portions of wax or tallow are continually melted. There is always a little cup of oil at the top of the rod of wax or tallow of which the candle consists, and the apparatus is as truly an oil-lamp as if the oil were held in a vessel of glass or metal.

If the flame of the candle, when the snuff has become long, be blown out, a current of vapor continues to ascend from the hot wick and this vapor may be ignited some distance above the wick. After the flame has been extinguished, the wick retains heat enough for a few moments to distil off a quantity of gas, although there is not heat enough generated to inflame this gas. To the gas or vapor thus evolved is to be referred the disagreeable odor which is observed when a candle is blown out.

Exp. 87. — Press down a piece of white letter-paper, for an instant, upon the flame of a candle until it almost touches the wick, then quickly remove the paper before it takes fire, and observe that its upper surface is charred in the manner shown in Fig. 45. There will be obtained, in fact, burned into the paper, a diagram of the part of the flame where combustion is taking place. It is thus seen to be ring-shaped in section, and to enclose a space where no combustion is going on.

Fig. 45.

203. All flames, which are rendered luminous by incandescent carbonaceous particles, have the same general structure. This structure is best studied in the flame of a candle.

In the candle-flame four portions or divisions of the flame can be distinguished (Fig. 46). First, there is the small blue cup-shaped portion of the flame (*a b*) at the base of the wick ; here a part of the combustible gases coming from the wick are burned completely, as the oxygen of the air has free access to this part of the flame. The heat thus produced converts into vapor the oil which the wick draws up

from the candle. This carbonaceous vapor rises and forms the second part of the flame, the non-luminous cone (*c*). Here no combustion can take place: the oxygen of the air, it is true, tends to pass, by diffusion, into the interior of the flame; but, as fast as it approaches, it meets carbon and hydrogen in the outer portion of the flame, and enters into combination with these elements: the nitrogen of the air, however, diffuses freely into the interior of the flame, and is found, mixed with the combustible gases of the candle and with some carbonic acid and steam, in the space (*c*).

Fig. 46.

The third portion of the flame is the luminous zone (*d*). Here the combustion is incomplete; the gaseous compounds of carbon and hydrogen are broken up by heat into their constituent elements. The carbonaceous particles are intensely ignited, and burn to carbon protoxide by taking oxygen from the air, and also from the carbonic acid and steam which diffuse inwards from the outermost portion of the flame.

The fourth portion of the flame is the thin, scarcely perceptible, non-luminous mantle (*f e f*) which surrounds the entire flame. Here the carbon protoxide and hydrogen burn to carbonic acid and steam, and, as has already been seen, a part of these gases diffuse inwards and are decomposed, furnishing oxygen for the partial combustion of the carbon in the luminous portion of the flame.

204. The principle of the **oxy-hydrogen blowpipe,** as well as of the ordinary blast lamps in which air and illuminating gas are used instead of oxygen and hydrogen, is the throwing of oxygen into the combustible gas so that the combustion is intense and concentrated. On the same principle depends the use of the **mouth-blowpipe.**

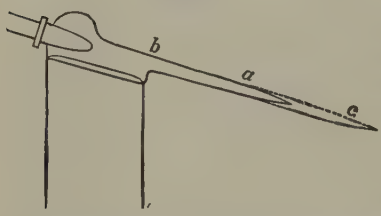
(For a description of the mouth-blowpipe, see Appendix, § 7.)

Exp. 88. — To use the mouth-blowpipe, place the open end of the tube between the lips, or, if the pipe is provided with a mouth-piece, press the trumpet-shaped mouth-piece against the lips; fill the mouth with air till the cheeks are widely distended, and insert the tip in the flame of a candle or of a lamp with a flat wick; close the communication between the lungs and the mouth, and force a current of air through the tube by squeezing the air in the mouth with the muscles of the cheeks, breathing, in the mean time, regularly and quietly

through the nostrils. The knack of blowing a steady stream for several minutes at a time is readily acquired by a little practice.

It is possible with the blowpipe to produce either an **oxidizing** or a **reducing** flame. When the jet of the blowpipe is inserted into the lamp or gas-flame, as shown in Fig. 47, and a strong blast is forced through the tube, a blue cone of flame (*a b*) is produced, beyond and outside of which stretches a more or less colored outer cone (*a c*). The point of greatest heat in this flame is at the point of the inner blue cone; oxidation takes place most rapidly at, or just beyond the point (*c*) of the flame, provided that the temperature at this point is high enough for the special substance to be heated.

Fig. 47.



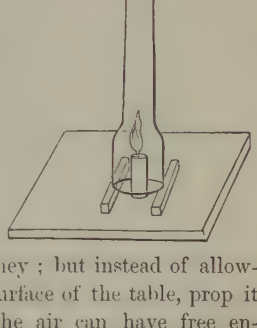
To obtain a good **reducing** flame, it is necessary to place the tip of the blowpipe, not within, but just outside of the flame, and to blow somewhat gently over rather than through the middle of the flame (Fig. 48). In this manner, the flame is less altered in its general character than in the former case, the chief part consisting of a large, luminous cone, containing a quantity of free carbon in a state of intense ignition and just in the condition for taking up oxygen. This flame is, therefore, **reducing** in its effect. The substance which is to be reduced by exposure to this flame should be completely covered up by the luminous cone, so that contact with the air may be entirely avoided.

Fig. 48.

205. Instead of forcing the air (or oxygen) into the burning fuel, the supply of air may be furnished by means of **chimneys.** Chimneys, whether of lamps or furnaces, are simply devices for bringing an abundance of air, and therefore of oxygen, into the fire; that in so doing they, at the same time, carry off the waste products of combustion is an incidental advantage.

Exp. 89. — Light a piece of a candle 8 or 10 c. m. long, and stand it upon a smooth table; over the candle place a rather tall, narrow lamp-chimney of glass, the bottom of the chimney being made to rest upon the table, and observe that the candle-flame will soon be extinguished. No fresh air can enter the chimney from below to maintain the chemical action, and the small quantity of air which can creep down the chimney from above is altogether insufficient to meet the requirements of the case.

Fig. 49.



Exp. 90. — Relight the candle of Exp. 89, and again place over it the lamp-chimney; but instead of allowing the chimney to rest closely upon the surface of the table, prop it up on two narrow strips of wood, so the air can have free entrance into the chimney from below. The candle will now continue to burn freely, for the heavy, cold air outside will continually press into the lower part of the chimney, and push out the warm, light products of combustion, and the candle-flame will all the while be supplied with fresh air.

The direction of the current of air may be shown by placing a piece of burning "touch-paper" at the foot of the chimney. Touch-paper is made by soaking ordinary brown paper in a strong solution of potassium nitrate, and then drying it. On being lighted, the paper burns without flame, while emitting clouds of smoke.

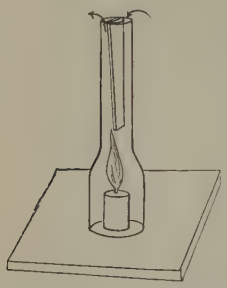
Exp. 91. — Repeat Exp. 90, and when the candle is burning quietly, cover the top of the chimney tightly with a piece of tin or sheet-iron, or with a strip of window-glass; the candle will soon cease to burn precisely as if the chimney were closed at the bottom, for, the escape of the hot products of combustion being prevented, no air can pass into the chimney to reach the candle-flame.

It is by inducing the current of fresh air (Exp. 90), or draught, as it is ordinarily termed, that chimneys are specially useful. Through the chimney the hot air from the lamp flows straight forward and rapidly, and, of course, a correspondingly direct and rapid current of fresh air presses in to supply its place. Owing to this power of rapidly supplying air, chimneys are employed upon lamps burning petroleum and other highly carbonized oils which are liable to smoke.

Exp. 92. — It is not absolutely necessary that the fresh air

should flow into a chimney from below. Divide the upper part of the chimney of Exp. 89 into two channels, by hanging in it a strip of sheet-iron or tin, as a partition at the centre of the chimney (see Fig. 50). Place the chimney thus divided over a burning candle, and observe that the candle will continue to burn as if in a strong draught of air, although no air can enter the chimney from below. Hold a piece of burning touch-paper at the top of the divided chimney; the smoke will be drawn down into the chimney on one side of the partition, and thrown out again upon the other, as indicated by the arrows in Fig. 50. It appears from this, as well as from the tremulous motion of the flame, that a current of cold air presses down upon one side of the division wall and supplies the required oxygen.

Fig. 50.



206. **Kindling-Temperature.** — In order that any combustible substance shall burn, or, in other words, in order that brisk chemical action shall occur between the combustible and the oxygen of the air, it must first be heated to a certain temperature, and then kept at that heat. The temperature at which any substance takes fire is known as the **kindling-temperature** of that substance.

Exp. 93. — Place a small bit of phosphorus and another of sulphur, not in contact with the first, upon a fragment of porcelain 6 or 8 c. m. across, and heat them slowly over the gas-lamp; the phosphorus will soon take fire at a temperature of 68°–70°, but the sulphur will not inflame until the temperature of the porcelain support has risen to about 250°, as can be ascertained by the thermometer.

As was just now said, the degree of heat necessary to start any fire must be kept up continually, or the fire will go out. Whenever burning bodies are cooled below the kindling-temperature, they are extinguished, — the chemical action which occasioned the appearance of heat and light ceases.

If we pile up upon an iron grate, thick in metal, and supported in such manner that air may enter beneath it, several pieces of red-hot

charcoal, the charcoal will go on burning until nearly all of it has been consumed, for the heat generated by the combustion of the portions first burned keeps up the temperature necessary to kindle the subsequent portions. If, however, we scatter about upon a cold grate several small pieces of red-hot charcoal, taking care that no two pieces of the coal shall come in contact, or be placed so as to heat one another, each of the pieces of charcoal will soon cease to burn ; for the metallic grate is so good a conductor of heat that it removes heat from the isolated pieces of charcoal more rapidly than these can produce it : the temperature of the charcoal is, consequently, soon reduced to below the kindling-point.

207. Precisely as coals can be extinguished by placing them upon cold metal, so flames may be put out.

Exp. 94. — Upon a ring of the iron-stand place a sheet of clean wire-gauze about 10 c. m. square ; lower the ring so that the gauze shall be pressed down upon the flame of a lamp or candle almost to the wick, as shown in Fig. 51. No flame will be seen above the gauze, but instead of flame a cloud of smoke. The gauze is a mere open sieve ; there is nothing about it which can prevent the gas, which was just now burning with flame above the wick of the candle, from passing through. Indeed, it may be seen from the smoke that the particles of carbon which, in the original undisturbed flame, were becoming incandescent, and so affording light, do now actually come through the gauze.

Fig. 51.

The explanation of the phenomenon is simply that the metallic sieve conducts away so much heat that the temperature of the candle-flame is reduced to below the kindling-point. That this is really so, is proved by the fact, that after the gauze has become sufficiently heated by long-continued contact with the flame below, — after it has attained the kindling-point of the candle-gas, — it will no longer extinguish the flame. In like manner, a candle-flame may be cooled to such an extent that it will go out by placing over it a small coil of cold copper wire, while, if the wire be previously heated, the flame will continue to burn.

If the smoke and unburned gas which has passed through the cold wire-gauze be touched with a lighted match, and so brought to the kindling-temperature, it will burst into flame.

The power of wire-gauze to prevent the passage of flame has been usefully applied in several ways, notably for the prevention of explosions in those coal-mines which are liable to accumulations of marsh-gas (§ 215). For this purpose safety-lamps are constructed by enclosing an ordinary oil-lamp completely in wire-gauze, so that the flame within the gauze can not kindle any combustible or explosive gas into which it may be carried. In case such a lamp be carried into a place filled with explosive gas, the latter will, of course, pass into the lamp through the meshes of the gauze, and burn within the cage. This combustion gives warning of the presence of the dangerous gas, and indicates to the workman that he should withdraw from the locality : the gas can then be expelled by appropriate methods of ventilation.

Exp. 95. — Beneath a sheet of wire-gauze resting on a ring of the lamp-stand, place an unlighted Bunsen's burner, at such a distance that the gauze shall be 3 or 4 c. m. above the top of the lamp ; turn on the gas and light it above the wire-gauze : it will continue to burn on top of the gauze for an indefinite period, for the gauze will, in this case, always be kept cool by the cold gas which is continually passing through it. Carefully and gradually lift the ring which carries the gauze, and determine how far it is possible to lift the gauze above the gas-jet without extinguishing the flame.

Fig. 52.

An effect somewhat similar to that produced by wire-gauze is often seen in ordinary fires. When a mass of red-hot anthracite, charcoal or coke is burning freely upon a grate in the open air, there is always a blue flame of carbon protoxide burning above the coal. This gas results from the reduction of carbonic acid by means of hot carbon. Air enters at the bottom of the grate and combines with the hot coal which it finds there to form carbonic acid, CO_2. This carbonic acid, as it rises through the hot coal in the middle of the fire, is deprived by the heated carbon of half its oxygen : $CO_2 + C = 2\,CO$. The carbon protoxide being combustible, will at once take fire on coming in contact with the air, provided the temperature at the summit of the fire be equal to the kindling-temperature of this gas. But if the temperature of the fire is in any way reduced below this point, as, for example, by throwing on too large a quantity of cold fuel, which is, of course, equivalent to covering the fire with a sheet of wire-gauze, then the carbon protoxide will be extinguished, and, escaping into the chimney, will produce no useful effect.

208. **Carbon and Sulphur.** — **Carbon bisulphide** (CS_2) is interesting from its correspondence to **carbonic anhydride,** CO_2, and forms another instance of the analogy between the compounds of oxygen and sulphur. Carbon bisulphide is prepared by passing the vapor of sulphur over red-hot charcoal. It is a colorless, strongly-refracting liquid which boils at about 54° and evaporates rapidly at the ordinary temperature of the air. It possesses an ethereal odor when purified, but the common bisulphide has a peculiar and very disagreeable smell. It is very inflammable and burns with a blue flame, the product of the combustion being carbonic and sulphurous anhydrides. It is used as a solvent of phosphorus and sulphur, and is employed in the cold process of vulcanizing caoutchouc.

Exp. 96. — Into a small beaker or watch-glass put two teaspoonfuls of carbon bisulphide. Set the glass upon a wet piece of wood, and by means of a glass tube direct a current of air from the lungs, or from a pair of bellows, across the surface of the liquid. The volatile carbon bisulphide rapidly evaporates, and in so doing produces such an amount of cold, that the glass will be frozen to the wood. This experiment should be performed where there is a good draught of air, and out of the neighborhood of any lighted lamp.

CHAPTER XV.

CARBON (continued).

209. **Carbon** unites with hydrogen, oxygen or nitrogen, or with two of these elements, or with all three of them, in the most varied proportions. A great number of different compounds are thus formed, some of them being extremely complex. Since many of these more complex compounds of carbon occur ready formed in animals and plants, or are produced by the transformation of substances derived from these sources, they are usually classed together and studied under the head of **"Organic Chemistry."**

There is no sufficient reason, chemically speaking, for making this division : chemical compounds, whether derived from the animal, vegetable or mineral kingdoms, are governed by the same laws : it is, moreover, impossible to draw any sharp line of demarcation between organic and inorganic chemistry ; still, on account of the vast number of the carbon compounds, the mere names of which would fill a volume, this arrangement has the merit of convenience. In this and the two following chapters a few of the more important of these so-called organic bodies will be considered.

Other elements besides those already mentioned, such as sulphur and phosphorus, enter into the composition of these bodies. Many of the complex substances which exist in the bodies of animals, such as albumin and the matter which forms the substance of the hair, contain sulphur as an essential ingredient. Moreover, the numerous *organic* acids form salts of the various metals, and many of these salts exist ready formed in nature.

210. **Carbon and Nitrogen.**—Prominent among the compounds of carbon and nitrogen is **cyanogen** (**CN**), which is an important compound radical, and which also exists in the free state.

211. **Cyanogen** (**CN** or **Cy**).—Carbon and nitrogen do not unite directly, but when a current of nitrogen is passed over red-hot charcoal which has been previously soaked in a solution of potassium carbonate, there is formed **potassium cyanide,** a compound containing the radical **cyanogen.**

$$K_2CO_3 + 4\,C + 2\,N = 2\,KCN + 3\,CO.$$

Free Cyanogen is best prepared by heating mercuric cyanide ; thus,—$HgCy_2 = Hg + 2\,Cy$. It is a colorless, poisonous gas of suffocating odor and ready inflammability. Its molecule contains two atoms of the radical and is written $(CN)_2$.

212. **Cyanhydric Acid** (**HCN**).—Cyanhydric acid, which may be prepared by passing hydrogen sulphide over mercury cyanide ($Hg(CN)_2 + H_2S = HgS + 2\,HCN$), is a combustible and volatile liquid : it possesses the odor of bitter almonds and is intensely poisonous. In aqueous solution it is known as **prussic acid.**

Several of the **cyanides** are important bodies, and will be mentioned under the head of the different metallic elements.

They correspond in composition to the **chlorides,** the univalent radical (§ **154**) **CN** occupying the place of **Cl**; thus potassium cyanide is **KCN**; zinc cyanide is $Zn(CN)_2$.

Exp. 97. — To a *very minute* quantity of solid potassium cyanide, add a few drops of strong sulphuric acid. The effervescence which takes place is due to the escape of cyanhydric acid, which may be recognized by its peculiar odor. The reaction is similar to that which takes place when common salt is treated with sulphuric acid in the production of chlorhydric acid. It may be expressed as follows: $2\,KCN + H_2SO_4 = K_2SO_4 + 2\,HCN$.

The **cyanates** correspond to **cyanic acid** (**HCyO**). Thus, potassium cyanate is **KCyO**.

213. **Compounds of Carbon and Hydrogen or Hydrocarbons** are very numerous. We first consider one of the most familiar of them, **marsh-gas.**

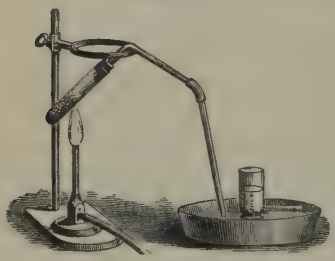
214. **Methyl Hydride or Marsh-Gas** (CH_4). — In hot summer weather bubbles of gas are often seen rising to the surface of stagnant pools: if a pole be thrust into the mud at the bottom of the pool, a considerable amount of the gas will rise and may be collected by holding an inverted bottle full of water over the ascending bubbles. The gas thus collected contains a certain amount of carbonic acid (which may be removed by putting some milk of lime into the bottle, and shaking it for a short time), together with a little nitrogen: the greater part, however, consists of a colorless gaseous compound of carbon and hydrogen. This gas is a product of the putrefaction of vegetable matter under water, where the supply of air is insufficient to oxidize the whole of the organic matter to carbonic acid and water; hence the name **marsh-gas.**

The formula of marsh-gas is CH_4, and it may be regarded as a compound of hydrogen (**H**) with a group of atoms (CH_3) called **methyl.** This group of atoms (CH_3) like the group (NH_4) which has been designated as **ammonium** (§ 67), and like **cyanogen** (§ 211), takes part in chemical transformations as if it were a simple elementary atom. The chemical name of marsh-gas is **methyl hydride,** or **methane.**

215. **Methyl hydride** forms a very considerable portion of ordinary illuminating gas made by distilling coal; from some varieties of bituminous coal, it is disengaged at the ordinary temperature, and forms the "fire-damp" of coal-mines; like hydrogen, it forms an explosive mixture with air, and the explosion of this mixture in badly-ventilated mines is often the cause of frightful loss of life. The gas may be prepared artificially as follows: —

Exp. 98. — Mix together two grms. of crystallized sodium acetate, 4 grms. of caustic soda and 8 grms. of slaked lime. Heat the mixture gently upon an iron plate, until all the water of crystallization of the acetate has been expelled, and the mass has become dry and friable. Charge an ignition-tube 20 c. m. long with the dry powder,

Fig. 53.



heat it above the gas-lamp, and collect the gas at the water-pan. Marsh-gas is evolved from the mixture, at a temperature below redness, and a residue of sodium carbonate is left in the ignition-tube. The purpose of the lime is to render the mass porous and infusible, or nearly infusible, so that the tube may be heated equably. The reaction may be represented as follows: —

$NaC_2H_3O_2$	+	$NaHO$	=	CH_4	+	Na_2CO_3.
Dry sodium acetate.		Sodium hydrate.		Marsh-gas.		Sodium carbonate.

216. **Marsh-gas** is transparent, colorless and little more than half as heavy as air. Next to hydrogen it is the lightest known substance, its specific gravity being only 8. It takes fire readily when touched with a lighted match, and burns with a bluish-yellow flame.

217. That marsh-gas really contains hydrogen and carbon may be readily proved by bringing into play, under appropriate conditions, the strong affinity of chlorine for hydrogen.

Exp. 99. — Fill a tall bottle of at least one litre capacity with warm water, invert it over the water-pan, and pass marsh-gas into it, until a little more than one-third of the water is displaced; cover

the bottle with a thick towel, to exclude the light, and then fill the rest of the bottle with chlorine. Cork the bottle tightly, and shake it vigorously, in order to mix the gases together, keeping the bottle always covered with the towel. Finally, open the bottle and apply a light to the mixture. Ignition takes place, chlorhydric acid is produced, while the sides and mouth of the bottle become coated with solid carbon in the form of lamp-black. The presence of the acid may be proved by the smell, by its reaction with moistened blue litmus-paper, and by the white fumes which are generated when a rod moistened with ammonia-water is brought in contact with the escaping acid gas.

218. **Chloroform** ($CHCl_3$). — When chlorine is allowed to act slowly on marsh-gas, there is formed, besides carbon quadrichloride (CCl_4), a compound having the formula $CHCl_3$ and called chloroform. Chloroform ($CHCl_3$) may be regarded as marsh-gas, in which three atoms of hydrogen have been replaced by three atoms of chlorine. It is manufactured in practice by distilling dilute alcohol with "chloride of lime." Water and chloroform come off together, but do not mix in the receiver: the chloroform, being the heavier, sinks to the bottom, and may be withdrawn and purified. Chloroform is a colorless, volatile liquid, the vapor of which when inhaled causes temporary insensibility to pain, and on this account it is used in surgical operations.

219. **Illuminating Gas.** — The principle involved in the manufacture of illuminating gas has already been illustrated in **Exps. 65** and **66**. Illuminating gas is ordinarily prepared by distilling bituminous coal; other substances made up wholly or in part of compounds of hydrogen and carbon, such as wood, oil, resin, petroleum and even bones, are sometimes used. **Fig. 54** shows in a general way the processes involved in the manufacture and purification of coal-gas.

The coal is introduced into the retorts, C, which are cylindrical or semi-cylindrical tubes of clay or iron, arranged in sets of three or five, or even more, and heated by a coke fire burning on the grate-bars, A. All the products of the distillation, except the coke which remains in the retort, are volatile at the high temperature employed, and pass up the vertical pipe, T. The relative proportions of these products, and to a certain extent their character, depend on the quality of coal employed, and on the temperature at which the dis-

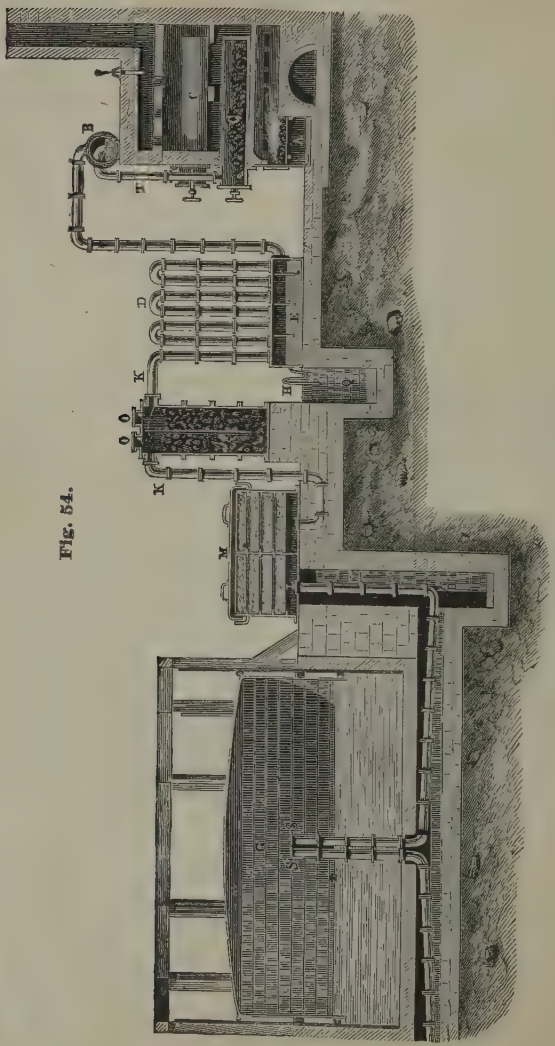


Fig. 54.

tillation takes place : it may, however, be said in general terms that these products, when cooled to the ordinary temperature, are of three kinds, — solid, liquid and gaseous.

The *gases* obtained by the distillation of coal are marsh-gas, olefiant-gas (§ 259), carbon protoxide, carbonic acid, hydrogen, nitrogen, aqueous vapor and hydrogen sulphide ; the liquid portion of the distillate consists of an aqueous solution of ammonium carbonate, sulphide and sulphocyanide, certain liquid hydrocarbons, such as benzol, toluol etc., which will be considered hereafter (§ 264), and a semi-liquid or viscous *tar*. The solid product of the distillation of coal is the *coke* left in the retort.

In the production of gas, all the volatile products of the distillation go up the pipe, T, which is curved at its upper extremity, and dips into water in the "hydraulic main," B. In this water a portion of the tar and aqueous vapor is condensed, and the ammoniacal salts are, in part, dissolved. The gas then passes alternately up and down through the cooling pipes, D, called the "condensers," and suffers further condensation, the remaining tar and the liquid hydrocarbons being deposited. The gas is often further purified by passing through a tower, O, filled with fragments of coke, over which water trickles, the water absorbing the ammoniacal salts still present. The gas then passes through the purifier, M, where it comes in contact with slaked lime and is freed from hydrogen sulphide and most of its carbonic acid, and thence into the gas-holder, G. The lime in the purifiers is sometimes replaced wholly or in part by dry ferric hydrate, which retains the hydrogen sulphide.

220. After purification, the gas as delivered to the consumer consists mainly of marsh-gas, hydrogen and carbon protoxide, — the marsh-gas usually amounting to about one-third part of the whole gas. These non-luminous, or very feebly luminous gases, serve as carriers of the six or seven per cent of real light-producing ingredients which are contained in the gas. This mixture of light giving ingredients is exceedingly complex. The vapor of benzol, no doubt, plays a prominent part ; some of the higher members of the marsh-gas series lend their aid, and a hydrocarbon of composition C_2H_2, called acetylene, is important and very generally present. Sometimes a little olefiant gas (C_2H_4) is present, but the old view, that this substance constitutes the chief luminiferous ingredient of coal-gas, is no longer admitted.

The *coal-tar* obtained as a waste product in the gas manufacture is a very complex substance. Among other substances it contains *benzol*, used in the manufacture of aniline colors, and *aniline* itself in very small proportion ; from it is obtained the *pitch* used as a roofing material and for sidewalks.

221. **Marsh-gas** is the first of a series of hydrocarbons, each member of which differs in formula from the preceding one by CH_2. This series may be arranged in tabular form, as follows : —

Marsh-gas Series.

Name.			Formula.			Boils at about
Methyl Hydride,	or	**Methane.**	CH_3,H	=	CH_4	[a gas]
Ethyl "	or	**Ethane.**	C_2H_5,H	=	C_2H_6	[a gas]
Propyl "	or	**Propane.**	C_3H_7,H	=	C_3H_8	[a gas]
Butyl "	or	**Butane.**	C_4H_9,H	=	C_4H_{10}	0
Amyl "	or	**Pentane.**	C_5H_{11},H	=	C_5H_{12}	37
Hexyl "	or	**Hexane.**	C_6H_{13},H	=	C_6H_{14}	68
Heptyl "	or	**Heptane.**	C_7H_{15},H	=	C_7H_{16}	98
Octyl "	or	**Octane.**	C_8H_{17},H	=	C_8H_{18}	128
Nonyl "	or	**Nonane.**	C_9H_{19},H	=	C_9H_{20}	148

It will be observed, that, while each member differs from the preceding one by CH_2, there is a difference of about 30° in the boiling-points of successive members. Many of the hydrocarbons of this series occur in the " coal-oil " obtained by distilling bituminous coals and shales at low temperatures, and also in petroleum.

222. **Petroleum** (literally, *rock-oil*) is a not uncommon natural product found in various parts of the world. In some cases it rises to the surface of the earth, but it is generally obtained by sinking wells into the rock strata in which it occurs. On this continent it is already found in large quantities in Pennsylvania and in Canada. In some of the wells the oil rises to the surface, being forced out by the marsh-gas which accompanies it ; in other cases, the oil does not reach the surface, and must be pumped out.

223. **Petroleum** is a thick, greenish, oily liquid of somewhat varying composition. The Pennsylvania petroleum is mainly a mixture of hydrocarbons of the marsh-gas series from C_4H_{10} to C_9H_{20}, together with other hydrocarbons of high boiling-point belonging to the so-called olefiant gas series (§ **259**). Marsh-

gas itself, as has been stated, accompanies petroleum, and in some localities, notably in Pennsylvania and in New York State, it issues from the ground in such large quantities that it is used to produce light and heat not only in household but also in metallurgical and other manufacturing operations.

224. Just as marsh-gas was regarded as the hydride of a radical methyl (CH_3), so the other members of the series may be regarded as hydrides of other radicals, ethyl (C_2H_5), propyl (C_3H_7), etc. These radicals are *univalent* (§ 154), and when they are obtained in the free state, they form molecules built on the type of free hydrogen (H_2): thus free ethyl is $(C_2H_5)_2$. Besides forming hydrides, these radicals enter into a variety of other compounds in which they replace hydrogen atom for atom. Among these compounds are the hydrates. These hydrates are formed on the type of water and correspond in formula to the hydrates of sodium and potassium, bodies already somewhat familiar.

Water.	Potassium hydrate.	Ethyl hydrate.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}K\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_2H_5)\\H\end{matrix}\right\}O$

The hydrates of these radicals may be obtained from the hydrides in a somewhat indirect manner; they are, however, ordinarily obtained from other sources, as will appear hereafter. Ethyl hydrate is ordinary **alcohol** (the formula, $(C_2H_5)HO$, representing the strongest or *absolute* alcohol). We now proceed to learn something of the preparation and properties of this important derivative of one of the members of the marsh-gas series.

225. **Alcohol** (C_2H_5,HO). — When the juices of plants or of fruits containing sugar, such as the juice of the grape, are kept for some time at a temperature of 20°, a peculiar change takes place. The liquor begins to *work*, bubbles of carbonic acid (CO_2) are given off, and it will be found, finally, that the sweet taste of sugar has disappeared, and that the solution now has a new smell and taste; by the **fermentation**, the sugar has been converted into carbonic acid and **alcohol**. The same change may be brought about in a simple solution of grape-sugar under the influence of yeast (**Exp. 79, § 193**).

Yeast is a collection of organized bodies, a sort of fungus or low

form of vegetable life. This fungus is made up of cells which grow and multiply in the fermenting liquid, and its existence in a liquid seems to be a necessary condition of fermentation. The apparently spontaneous fermentation which takes place in the juice of fruits is explained by supposing that the *spores* or germs of such a plant are introduced from the air, the decay of certain albuminous matters in the juice furnishing favorable conditions for the reception and growth of the fungus.

226. **Alcohol** is a colorless, volatile and inflammable liquid, lighter than water and capable of mixing with it in all proportions.

The volatility and inflammability of alcohol have already been illustrated in Exp. 84, § 202. The production of alcohol as a result of fermentation may be illustrated by a repetition of Exp. 79, § 193 under somewhat different conditions, as follows : —

Fig. 55.

Exp. 100. — Dissolve 30 grms. of grape sugar in 400 c. c. of water, and with the solution fill a flask of 350 or 400 c. c. capacity nearly to the neck. Add two or three teaspoonfuls of fresh brewers' or bakers' yeast, and then connect the flask with a bottle filled with water, as represented in Fig. 55. Put the whole apparatus in a warm place. Fermentation will soon set in, and bubbles of carbonic acid will be seen rising through the liquid. As this gas collects in the upper part of the flask, it will pass over into the small bottle, and force out a corresponding amount of water. When the bottle is full or partly full of the gas, remove the stopper, and prove the presence of carbonic acid either by means of a burning match, which will be extinguished (Exp. 76, § 190) or by means of lime-water, which will be rendered turbid (Exp. 73, § 188). Allow the liquid in the flask to remain in a warm place for about 48 hours, when the sweet taste of the sugar will be found to have wellnigh disappeared as the sugar will have been converted mainly into alcohol and carbonic acid.

This experiment may be performed equally well by substituting 45 or 50 grms. of sirup for the 30 grms. of grape sugar.

227. To separate the alcohol from the liquid in which it has

been formed by fermentation, the liquid is subjected to distillation. The boiling-point of alcohol is about 20° lower than that of water, and consequently all the alcohol will be found in the first portion of the distillate. By several successive distillations the alcohol may be obtained nearly pure.

Exp. 101. — Pour off one-half of the fermented liquor of Exp. 100, and reserve it for Exp. 106; with the remainder proceed as follows: Support the flask on the iron lamp-stand, and, by means of a delivery-tube of No. 6 glass, connect it with a second flask capable of holding one-third of the liquid and placed on a water-bath, as represented in Fig. 56. From this second flask a delivery-tube is carried to a small flask kept cool by immersion in cold water. Heat the liquid in the largest flask, so that it just boils: the vapor of alcohol, together with a certain amount of steam, passes into the second flask, which is kept just below the boiling-point of water by being supported on the water-bath in which the water barely boils. At this temperature a considerable portion of the alcohol, together with some water, passes over into the third flask, where it is condensed. Continue the operation until about one-third of the liquid has passed out of the large flask. The liquid obtained in the third flask is a dilute alcohol; the odor of alcohol is distinctly perceptible, but the alcohol may not be strong enough to burn. In that case support the third flask on the wire-gauze over the lamp, and connect it by means of a delivery-tube with another small flask, which is kept cool. Heat the contents of the flask gently until they just boil, and transfer the first teaspoonful of the liquid which condenses in the cooled flask to a porcelain dish. If the experiment has been successfully conducted, the alcohol thus obtained will be strong enough to take fire if a flame be brought into contact with it.

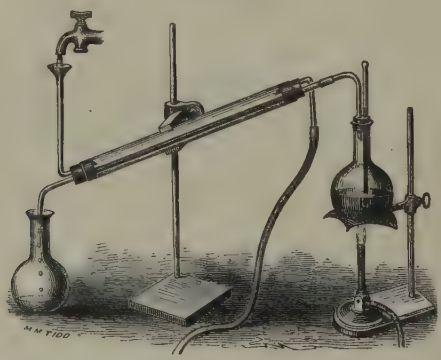
Fig. 56.

The alcohol obtained by successive distillations of a dilute alcoholic liquid still retains a certain amount of water. This

water may be removed by adding quick-lime, a substance which has a great attraction for water, and distilling the mixture. Alcohol perfectly anhydrous is called **absolute alcohol**. Exposed to the air, it attracts moisture. Ordinary strong alcohol contains about 10 per cent of water.

228. Exp. 101 affords an excellent example of what is known as **fractional distillation**. When the boiling-points of several liquids differ by a considerable number of degrees, they may thus be separated from each other in a tolerable state of purity by observing the temperature of the boiling liquid and collecting by themselves the successive portions of the distillate which come off within certain narrow limits of temperature. In operating with very volatile liquids, it is well to interpose a cooling apparatus between the retort, or *still*, and the receiver. Fig. 57 contains a representation of the so-called Liebig's condenser alluded to in § 32.

Fig. 57.

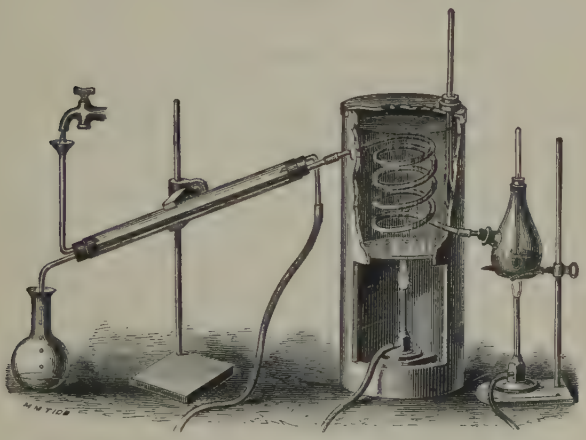


The manufacture of burning oil from crude petroleum is another example of fractional distillation. When petroleum is distilled, the first portion of the distillate consists of very volatile hydrocarbons known by the general name of *naphtha*. The less volatile compounds which next follow form the "*kerosene oil*" or "*petroleum oil*" of commerce. The frightful accidents arising from the use of kerosene are due to the fact that the oil is often imperfectly freed from, or purposely adulterated with, the more volatile and inflammable hydrocarbons. All these volatile hydrocarbons in the state of vapor form explosive mixtures with air; and such explosive mixtures are likely

to be formed in vessels or in lamps only partially full of the volatile liquids.

A modification of this process, "**fractional condensation,**" effects a more complete separation. In this process the vapors, after leaving the retort, pass upwards through an inverted "worm," the temperature of which is so regulated that the less volatile bodies are almost entirely condensed, and so made to flow back into the retort; while the more volatile vapors go forward, and are condensed in the usual way in appropriate receivers.

Fig. 58.



229. **Alcohol** is much used in the arts; it forms the basis of all fermented and distilled liquors; it is employed as a convenient fuel, and, when mixed with benzol, oil of turpentine or other hydrocarbons, for the production of light. It is also valuable as a solvent; it dissolves many substances such as resins and oils, which are insoluble in water: thus, shellac-varnish is an alcoholic solution of a peculiar resin known as shellac; the *tinctures* of pharmacy are alcoholic solutions of medicinal principles.

The formula of **absolute alcohol** is C_2H_6O. It may be regarded, as has been said, as a hydrate of the radical ethyl (C_2H_5), and may be written (C_2H_5) **HO**. As alcohol is a hydrate of ethyl, so there

are hydrates of each of the radicals of the marsh-gas series (§ 221); thus: —

			Boiling-point.
Methyl Alcohol	is	CH_3,HO or CH_4O,	66.5°
Ethyl	"	" C_2H_5,HO " C_2H_6O,	78.4
Propyl	"	" C_3H_7,HO " C_3H_8O,	97
Butyl	"	" C_4H_9,HO " $C_4H_{10}O$,	116
Amyl	"	" C_5H_{11},HO " $C_5H_{12}O$,	137
Etc.			

230. **Methyl Alcohol** (CH_3,HO) resembles ordinary (ethyl) alcohol in being a light, colorless, inflammable liquid. It resembles alcohol also in its solvent powers, and is used in its stead for many purposes, such as dissolving shellac. It is prepared by the destructive distillation of wood (§ 282), and ordinarily contains certain impurities, which give to it an empyreumatic odor. It is commonly known as **wood-spirit.** *Methylated spirit* is ordinary alcohol, to which a certain amount of methyl alcohol has been added; this addition does not interfere with the use of the alcohol for many purposes to which it is applied in the arts, but renders it unfit for drinking.

231. **Amyl Alcohol or Fusel Oil** (C_5H_{11},HO) is a colorless liquid of disagreeable odor. It will not mix with water, and is not readily inflammable. It is formed in the manufacture of brandy and whiskey from potatoes and grain, and, as it has a boiling-point much higher than that of ordinary alcohol, it may be separated from alcohol quite completely by the method of fractional distillation. Fusel oil burns with a somewhat smoky flame, and is principally used for purposes of illumination.

232. **Ether.** — When a mixture of strong sulphuric acid and alcohol is heated in a retort, there distils over with water, a highly volatile, inflammable liquid known as **ether.** The distillate, which must be condensed in a well-cooled receiver, separates into two layers; the ether being almost insoluble in the water and lighter than it, forms the upper layer, and may be drawn off nearly free from water. The last portions of water are removed by allowing the ether to stand over quick-lime, and then distilling.

The reaction between the sulphuric acid and alcohol may be represented as taking place in two stages : —

(1.) $(C_2H_5)HO$ + H_2SO_4 = $H(C_2H_5)SO_4$ + H_2O.
Alcohol. Sulphuric acid. Hydrogen Ethyl sulphate. Water.

(2.) $H(C_2H_5)SO_4$ + $(C_2H_5)HO$ = $(C_2H_5)_2O$ + H_2SO_4.
Hydrogen Ethyl sulphate. Alcohol. Ether. Sulphuric acid.

The alcohol and sulphuric acid are mixed in equivalent proportions, and as the water and ether distil off, the loss is supplied by a stream of fresh alcohol flowing slowly, but without interruption, into the retort. The operation thus goes on continuously.

Exp. 102. — Into a small test-tube put 10 drops of ordinary alcohol and as much strong sulphuric acid, and heat the mixture gently over the lamp. Ether will be formed, and may be recognized by its peculiar odor.

The student should never attempt to perform any experiment requiring more than a very minute quantity of ether, since it is highly dangerous to work with this substance on account of its great volatility, and ready inflammability.

233. Ether is a colorless, very mobile, volatile liquid : it possesses a powerful odor, and, when inhaled, produces insensibility to pain ; hence it is used in surgical operations. The vapor of ether is very heavy and exceedingly inflammable, and in certain proportions forms an explosive mixture with air.

Exp. 103. — Pour a small quantity of ether into the palm of the hand, and observe the rapidity with which it evaporates, and also the cold produced by this evaporation.

Exp. 104. — Into a tumbler or other very wide-mouthed vessel put a few drops of ether. Cover the vessel loosely, and allow to stand for a few moments ; then bring a lighted match to the mouth of the vessel : the heavy vapor of ether will have displaced the air in the vessel, and will take fire at the mouth of the vessel with a sudden flash.

234. Ordinary ether ($(C_2H_5)_2O$) is an oxide of the radical ethyl (C_2H_5). The corresponding oxides of the other radicals of the marsh-gas series are classed together under the general name of ethers ; thus : —

Methyl	**oxide**	or	**Methyl**	**Ether**	is $(CH_3)_2O$ or C_2H_6O
Ethyl	"	"	**Ethyl**	"	" $(C_2H_5)_2O$ " $C_4H_{10}O$
Propyl	"	"	**Propyl**	"	" $(C_3H_7)_2O$ " $C_6H_{14}O$
Butyl	"	"	**Butyl**	"	" $(C_4H_9)_2O$ " $C_8H_{18}O$
Etc.					

As these hydrocarbon radicals, methyl, ethyl, propyl, etc., unite with hydrogen to form *hydrides*, with oxygen to form *oxides* (ethers), and with hydrogen and oxygen to form *hydrates* (alcohols), so they can form *salts* corresponding to the various acids. The formulæ of these salts may be written by replacing the hydrogen of the acid by the different radicals. Thus ethyl sulphate is $(C_2H_5)_2SO_4$; ethyl nitrate is $(C_2H_5)NO_3$; methyl chloride is CH_3Cl; propyl sulphide is $(C_3H_7)_2S$; and so on. In the case of an acid like H_2SO_4 containing two replaceable atoms of hydrogen, there can be formed bodies like hydrogen ethyl sulphate $H(C_2H_5)SO_4$ corresponding precisely to hydrogen potassium sulphate, $HKSO_4$.

Mercaptans. — Among the compounds of the radicals of the marsh-gas series, may be mentioned the mercaptans. These compounds correspond in formula to the alcohols, except that the oxygen is replaced by sulphur: they may be regarded as derived from hydrogen sulphide, in the same way that alcohol is derived from water.

Water.	Ethyl alcohol.	Hydrogen sulphide.	Ethyl mercaptan.
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\H\end{matrix}\right\}S$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S$

The salts of the various radicals are often called **compound ethers**; methyl chloride is called methyl-chlorhydric ether, ethyl sulphate is called ethyl-sulphuric ether, or simply sulphuric ether. (The term "sulphuric ether" is sometimes used to denote ordinary (ethyl) ether. This designation is, however, improper, as ordinary ether contains no sulphur whatever.) Several of these compound ethers are manufactured in large quantities for the preparation of perfumery and flavoring extracts. Thus amyl acetate, or amyl-acetic ether (made from fusel oil), has the odor and taste of the jargonelle pear; amyl valerianate has the smell and taste of apples, and is known as *apple-oil;* ethyl butyrate has the flavor of pine-apples, etc.

The preparation of one of these compound ethers, ethyl acetate, may be illustrated by the following experiment.

Exp. 105. Into a small test-tube put 10 drops of ordinary alcohol, and the same amount of strong sulphuric acid. Add a crystal of sodium acetate as large as a small pea, and heat the mixture gently,

Acetic ether, ethyl acetate, is formed, and may be recognized by its peculiar odor.

235. **Acetic Acid** ($C_2H_4O_2$). — When the alcoholic liquid formed by the fermentation of the juice of grapes or other fruits is exposed to the air, it gradually becomes sour, and is eventually converted into vinegar. Under the influence of the oxygen of the air, the alcohol changes into **acetic acid.** Vinegar is a very dilute solution of this acid, containing about 2 to 4 per cent of the acid, together with coloring matter, and various other impurities derived from the juice of the fruit from which it is prepared.

Exp. 106. — Allow that portion of the alcoholic liquor of Exp. 100 which was not distilled to remain for a number of days in a loosely-covered vessel. The liquid will gradually become sour, and acquire the taste and smell of vinegar. The alcohol has been converted into **acetic acid**. Preserve this acid liquid for use in a subsequent experiment.

Vinegar, as has just been seen, may be produced by allowing an alcoholic liquid to become sour gradually, by exposure to the air in imperfectly-closed vessels. On the large scale, however, it is generally made by allowing the air to have access to weak alcohol, spread in a very thin layer over a very great surface. The operation is conducted in large casks filled with wood-shavings, over which the alcoholic liquid (as cider, whiskey or brandy diluted with water) slowly trickles. The cask is furnished with a false bottom, and with a head perforated with small holes, which serve to distribute the alcohol evenly over the shavings. Air enters the cask through holes, as at *a*, and escapes through the tubes (*c c c*), and through several holes in the cover of the cask. The liquid which runs out of the cask may be returned to the top, until, after passing through the cask several times, the alcohol is entirely converted into acetic acid. The cask may be made of such size, and the flow so regulated, that the conversion of the alcohol to vinegar is complete after one operation.

Fig. 59.

The chemical changes which take place are as follows : the alcohol under the influence of a little yeast, honey or grape sugar, with which it is mixed, has a great tendency to absorb oxygen from the air, and be converted into water, and a new compound, **aldehyde.**

$$\underset{\text{Alcohol.}}{C_2H_5,HO} + O = \underset{\text{Aldehyde.}}{C_2H_3O,H} + H_2O.$$

Aldehyde is an unstable compound which oxidizes very readily. As it passes over the shavings, the oxygen of the air comes in contact with it over a very great surface, and it is rapidly converted into acetic acid :

$$\underset{\text{Aldehyde.}}{C_2H_3O,H} + O = \underset{\text{Acetic acid.}}{C_2H_3O,HO}.$$

Aldehyde is a very volatile compound, and on this account, unless the supply of air furnished be abundant, a considerable loss of alcohol is experienced in this process.

236. **Chloral** or **Trichloraldehyde** (C_2Cl_3OH). — By replacing three atoms of hydrogen in the formula of aldehyde by as many atoms of chlorine, the formula of a body known as **chloral** is obtained. This compound is formed by passing chlorine through absolute alcohol. It is an oily fluid, which unites with a small quantity of water to form a crystalline hydrate, much used of late in medicine to induce sleep.

237. The formula of **acetic acid is** $C_2H_4O_2$ or, written on the type of water, $\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O$, an atom of hydrogen being replaced by a hypothetical oxygenated radical, C_2H_3O, called **acetyl.** This radical has not been isolated : its chloride, however, is known. If this hypothetical radical **acetyl,** C_2H_3O, be compared with **ethyl,** C_2H_5, it will appear that two atoms of hydrogen in the latter are represented by one atom of oxygen in the former. By the similar device

from		may be derived		the hypothetical radical of	
Methyl	CH_3	**Formyl**	CHO	**Formic acid**	CH_2O_2
Propyl	C_3H_7	**Propionyl**	C_3H_5O	**Propionic acid**	$C_3H_6O_2$
Butyl	C_4H_9	**Butyryl**	C_4H_7O	**Butyric acid**	$C_4H_8O_2$
Amyl	C_5H_{11}	**Valeryl**	C_5H_9O	**Valeric acid**	$C_5H_{10}O_2$
Etc.		**Etc.**		**Etc.**	

Acetic acid is thus one member of a series of acids ; they are called the **fatty acids,** and several members of the series are of very great industrial importance.

238. **Acetic acid** is one of the products of the distillation

of wood (§ **282**), and, thus obtained, it is known in the crude state as **pyroligneous acid.**

The pure acid is obtained by acting on some acetate, as sodium acetate, with sulphuric acid, and then distilling the mixture. At the ordinary temperature, acetic acid is a volatile liquid possessing a pungent odor, but at 17° it becomes a transparent solid; hence the name **glacial acetic acid** applied to the strongest acid.

Exp. 107.—To the acid liquid of Exp. 106, or to 40 or 50 c. c. of common vinegar, add powdered chalk (calcium carbonate) as long as the addition causes effervescence. Calcium acetate is formed and remains dissolved in the liquid. Filter the solution, and evaporate the filtrate to dryness at a gentle heat. The solid residue is an impure calcium acetate. Place a portion of this calcium acetate in a small test-tube, and heat gently with a few drops of strong sulphuric acid. Acetic acid will be set free, and may be recognized by its peculiar odor. If ordinary vinegar be used in this experiment, it will be better to decolorize the solution of calcium acetate by mixing it with powdered bone black before filtering (see Exp. 72, § 185).

The **acetates** are important bodies, and many of them are used in the arts and in medicine. Aluminum acetate is used in dyeing (§ 451); lead acetate is familiar under the name of *sugar of lead;* copper acetate is known as *verdigris;* ethyl acetate is *acetic ether.*

239. **Formic acid** (CH_2O_2), another member of the fatty acid series, is secreted by ants, and was first obtained by distilling the bodies of these insects: it bears the same relation to methyl alcohol (CH_4O) that acetic acid does to ordinary (ethyl) alcohol, and may be prepared by the oxidation of methyl alcohol. Formic acid is interesting because one of its salts, potassium formate, may be readily prepared from what are usually classed as inorganic substances.

If moist caustic potash be exposed to carbon protoxide at a temperature of 100°, the gas is slowly absorbed, and **potassium formate** is produced: from potassium formate thus made the acid itself may be indirectly obtained.

$$\begin{matrix} K \\ H \end{matrix}\Big\} O \quad + \quad CO \quad = \quad \begin{matrix} K \\ (CHO) \end{matrix}\Big\} O$$

Potassium hydrate. Carbon protoxide. Potassium formate.

Formic acid is one of a vast number of compounds which formerly were supposed to be produced only through the agency of living organisms, but which now can be made in the laboratory from inorganic substances. This synthetical construction of so-called organic substances has contributed to obscure the distinction formerly drawn between organic and inorganic chemistry.

240. One of the salts of formic acid will serve as an excellent illustration of the value of *rational* formulæ (§ 152). The formula of **methyl formate** ($C_2H_4O_2$) is the same as that of **acetic acid,** and the *empirical* formulæ afford no means of distinguishing between these two substances ; if, however, methyl formate be written $\left.\begin{matrix}(CHO)\\(CH_3)\end{matrix}\right\}O$ and acetic acid, as before, $\left.\begin{matrix}(C_2H_3O)\\H\end{matrix}\right\}O$ these formulæ represent to the mind two distinct bodies. As the properties of the two substances are very different, we naturally seek to account for such different manifestations of the same elements in the same proportions by imagining some difference in the arrangement of the atoms within the molecule ; and, although we cannot *know* what this arrangement is, we can recall by the rational formulæ some of the reactions which occur in the formation or the decomposition of the substances in question. Bodies which like acetic acid and methyl formate have the same ultimate composition are called **isomeric.**

Other acids of the fatty acid series will be brought to our notice by the study of a very important natural group of organic compounds, that of the fats and oils.

241. **Natural Fats and Oils.** — The various fats and non-volatile oils obtained from both the animal and the vegetable kingdom are in the main mixtures of three well-defined bodies, two of which, **stearin** and **palmitin,** are solid at the ordinary temperature, while the third, **olein,** is liquid.

Exp. 108 — Expose a test-tube full of olive-oil to cold by surrounding it with a mixture of salt and pounded ice. A portion of the oil solidifies, while another portion remains liquid. The solid portion is mainly palmitin, the liquid, olein.

Olive oil consists essentially of olein and palmitin ; beef-tallow is mainly stearin ; lard is made up of olein and palmitin ;

butter is olein, palmitin, together with several other peculiar fats, to which its taste and odor are due.

The chemical constitution of these bodies may be best represented by the use of typical formulæ. Stearin is a salt of **stearic acid**, and may be regarded as built upon the type of three molecules of water: its formula may be derived from that of stearic acid by substituting for three atoms of hydrogen in three molecules of the acid one atom of the trivalent radical **glyceryl** (C_3H_5), thus: —

Type.	Stearic acid. (Three molecules.)	Stearin. (One molecule.)
$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}(C_{18}H_{35}O)_3\\H_3\end{matrix}\right\}O_3$	$\left.\begin{matrix}(C_{18}H_{35}O)_3\\(C_3H_5)\end{matrix}\right\}O_3$

Stearin is **glyceryl stearate**; similarly palmitin is **glyceryl palmitate**, and olein is **glyceryl oleate**. Oleic acid does not belong to the same series with stearic and palmitic acids; but, from the association in nature of the oleates and the stearates, it is conveniently introduced in this connection.

242. The various fats and oils are insoluble in water; they are, however, readily dissolved by certain liquids, such as ether, benzol, oil of turpentine, etc.

Exp. 109. — Fill a small bottle half full of water, and pour in a few drops of olive-oil. The oil remains on the top of the water, and is not dissolved by agitating the mixture.

Exp. 110. — Into a small bottle put two teaspoonfuls of concentrated ether, and add one quarter as much olive-oil. Cork the bottle tightly, and shake it: the oil is readily dissolved by the ether.

243. **Manufacture of Soap.** — Very great industrial importance attaches to many of the natural fats and oils on account of their use in the manufacture of soaps and "stearine" candles; in both of these industries, a hydrate of glyceryl, **glycerin**, $\left.\begin{matrix}(C_3H_5)\\H_2\end{matrix}\right\}O_2$, is a secondary product.

The manufacture of **soap** may be illustrated by the following experiment: —

Exp. 111. — Dissolve 15 grms. of solid caustic soda in 120 c. c. of water. When the suspended impurities have settled to the bottom of the solution, pour off one half of the clear liquor into a deep iron

or porcelain dish of at least 500 c. c. capacity (see Appendix, § 21), add an equal bulk of water, and 50 grms. of beef tallow. Bring the mixture to boiling and boil it steadily for three quarters of an hour, supplying from time to time the water lost by evaporation ; then add the remainder of the solution of caustic soda, and continue to boil steadily for an hour or more, allowing the liquid to become somewhat more concentrated towards the end of that time ; then add 20 grms. of fine salt, boil for a minute or two, and allow the liquid to cool. A part of the mass becomes solid, and rises to the top ; it is **hard soap**.

The chemical action is thus explained : when tallow (glyceryl stearate and oleate) is boiled with sodium hydrate, there is formed sodium stearate (and oleate) and glyceryl hydrate. When common salt is added, the soap (sodium stearate and oleate), being insoluble in the saline liquid, separates as a solid. The liquid remaining contains in solution the excess of sodium hydrate employed, as well as the salt and the glycerin.

Soap may be made more quickly by using castor-oil instead of beef-tallow. Mix 100 c. c. of castor-oil and 100 c. c. of caustic soda solution prepared as above, and boil for 30 minutes. Then add 150 c. c. of water, bring to a boil, and add 20 grms. of salt. The soap rises to the top and may be removed when cold. Castor-oil is mainly glyceryl ricinoleate ; the chemical change is similar to that just described.

Exp. 112.—Heat some of the soap of Exp. 111 with soft water. A nearly clear solution will be obtained if the decomposition of the tallow or oil was complete. Add dilute chlorhydric acid until the solution is decidedly acid. The liquid will become turbid, and on standing, will become covered with a layer of a fatty substance which is a mixture of stearic and oleic acids (or mainly ricinoleic acid if castor-oil was used). The sodium chloride formed will be held in solution by the liquid.

Other **bases** besides caustic soda may be used to effect the decomposition of oils or fats. If **caustic potash** be used, a *soft soap* is formed ; if **slaked lime** be employed, there is formed a lime soap, **calcium stearate,** etc., insoluble in water ; if **lead oxide** be used, there results an insoluble lead soap used in medicine under the name of **lead plaster** or **diachylon.**

244. In **Exp. 111,** one of the products of the reaction, **glycerin,** remained dissolved in the solution of sodium chloride and hydrate. This substance may be prepared as follows ;—

Exp. 113. — Into a deep porcelain dish put 50 grms. of litharge and 75 c. c. water. Into this mixture stir 50 grms. of olive oil, and boil the mixture steadily for 50 or 60 minutes with constant stirring, and occasional addition of water to replace that lost by evaporation. The oil is gradually decomposed; an insoluble lead soap (lead plaster) is formed, and the color of the mass in the dish becomes lighter. When the oil seems to be entirely decomposed, pour off the liquid portion through a filter, add 50 c. c. of water to the lead plaster, boil for five minutes, and pass this liquid also through the filter. The glycerin is dissolved by the water, and with it passes through the filter. Evaporate the filtered liquid to dryness at a gentle heat: the glycerin will remain as a sirupy, non-volatile liquid, having a sweet taste. As the amount of glycerin obtained will be very small, it is well to transfer the solution when nearly evaporated to a watch-glass, and to finish the evaporation on a water-bath.

Glycerin, when pure, is a colorless, sweet-tasting, sirupy liquid, which mixes with water in all proportions. When heated in the air, it is slightly volatile, but cannot be distilled without decomposition, and the formation of vapors of **acrolein** very irritating to the eyes. This same substance is formed when fat burns, and is the cause of the peculiar odor given off from the smouldering wick of a tallow candle.

Glycerin is used somewhat in medicine, mainly for external applications: its use depends upon the fact that it is but slightly volatile, and does not dry up or undergo change when exposed to the air.

245. **Nitro-Glycerin** is an oily liquid heavier than water which is formed when glycerin is allowed to flow gradually into a cooled mixture of nitric acid and oil of vitriol. It is a highly explosive compound, being decomposed either by direct application of heat, or by percussion. It is used for blasting purposes instead of gunpowder, but is very dangerous to transport: the danger in using it can be very much lessened by making the nitro-glycerin immediately before use at the quarry or other locality where it is to be employed, or by impregnating with it some porous material. Dynamite, for instance, is infusorial earth thus impregnated.

The formula of nitro-glycerin is $\left.\begin{matrix}(C_3H_5)\\(NO_2)_3\end{matrix}\right\}O_3$, while that of gly-

cerin is $\left.\begin{matrix}(C_3H_5)\\H_3\end{matrix}\right\}O_3$; that is, three atoms of hydrogen have given place to three atoms of the radical *nitryl* (NO_2): nitro-glycerin may be regarded as *glyceryl nitrate.*

246. As has been stated, glycerin is also a product of the manufacture of what are known as stearine candles. These candles are not, properly speaking, stearin, but are made of the solid fatty acids; namely, stearic and palmitic. Any process by which stearin (and, of course, palmitin and olein) is decomposed, so that the fatty acid or glycerin, or both bodies, are set free, is termed **saponification,** even in cases where no soap results from the reaction.

By treating the fat with sulphuric acid, it may be decomposed with formation of the fatty acids and glycerin, and the two products can be readily separated from each other. The decomposition may also be effected by the use of superheated steam, and in the manufacture of candles these two methods are employed to a very large extent, although the fatty acids are sometimes obtained by first forming a lime soap and then decomposing it with acid, as the soda soap was decomposed in **Exp. 112.** The fatty acids are cooled and submitted to pressure, which separates the oleic acid: the solid acids are then moulded into proper forms.

Candles are also manufactured from spermaceti, paraffin and wax. Spermaceti is a solid fat obtained by cold and pressure from the oil of the sperm whale; when saponified, it yields palmitic acid and **ethal** ($C_{16}H_{34}O$). **Paraffin** is at ordinary temperatures a white solid having a pearly lustre. It is generally regarded as a mixture of several members of the marsh-gas series of hydrocarbons ($C_n H_{2n+2}$), which, indeed, are sometimes designated as the paraffin series or the paraffins. It occurs in petroleum, and when the petroleum is distilled, it comes off in abundance at the latter part of the distillation. It is separated from the accompanying liquid hydrocarbons by cold and pressure. Paraffin also occurs in smaller quantity among the products of the distillation of bituminous coal and wood. Beeswax is mainly a salt of palmitic acid, melissyl palmitate, together with a free acid, cerotic acid. Chinese wax, produced by an insect belonging to the same genus as the cochineal insect, yields on saponification two bodies, cerotin and cerotic acid: it is cerotyl cerotate.

247. **Artificial Fats.** — While by the various processes of saponification it is possible to obtain from the natural fats (with the elements of water) both glycerin and a fatty acid, it has also been found possible to reproduce the fats by bringing the fatty acids and glycerin together under appropriate conditions: in this case water is eliminated precisely as water was set free in the formation of potassium nitrate from caustic potash and nitric acid (Exp. 25, § 62).

Glycerin. Stearic acid. Stearin. Water.

$$\begin{matrix}(C_3H_5)\\H_3\end{matrix}\Big\}O_3 + 3\left[\begin{matrix}(C_{18}H_{35}O)\\H\end{matrix}\Big\}O\right] = \begin{matrix}(C_3H_5)\\(C_{18}H_{35}O)_3\end{matrix}\Big\}O_3 + 3\,H_2O$$

248. **Vegetable Oils.** — Of the oils and fats thus far considered, all, with two or three exceptions, have been of animal origin: all plants, however, contain some representative or representatives of this class. These vegetable fats and oils occur most abundantly in certain seeds and fruits, such as the seeds of hemp, flax, cotton, sunflower, and the kernels of the stone of the peach, also in such nuts as the peanut, butternut, beechnut, almond, etc. Oil occurs also in the cereals, as may be illustrated by the following experiment: —

Exp. 114. — Dry two or three teaspoonfuls of corn-meal on the water-bath for an hour or two. Put the dry meal into a small bottle and pour upon it twice its bulk of ether. Cork the bottle tightly and shake it from time to time during half an hour. Finally filter the liquid into a clean porcelain dish (taking care that there is no lighted lamp or fire in the vicinity), and place the dish where there is a good draught. The ether will evaporate spontaneously and a yellowish oil will remain.

All of these oils are called **fixed** oils: they leave a permanent greasy stain on paper, and cannot be distilled unchanged.

The fixed vegetable oils consist in great measure, like the animal fats, of stearin, olein and palmitin; but many of them contain other substances in greater or less proportion. Thus bayberry-tallow, a familiar example of a vegetable fat, consists in part of palmitin and palmitic acid, and in part of a substance known as *lauric acid*.

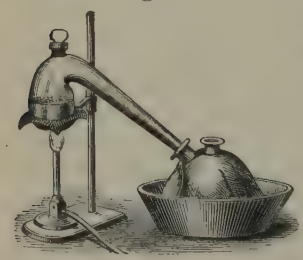
249. **Drying Oils.** — Certain oils, especially linseed oil, when exposed to the air, gradually absorb oxygen and become solid. Such oils are called *drying oils*. This absorption of oxygen

causes the evolution of a considerable degree of heat: in fact, cases of spontaneous combustion often occur from the taking fire of heaps of rags, tow or other light material, saturated or smeared with oil.

250. **Essential Oils.** — To be distinguished from the non-volatile or **fixed** oils are the volatile or **essential** oils. These compounds, in some points, resemble the fixed oils, — they are inflammable, insoluble in water and readily soluble in alcohol and ether: they are, however, more or less volatile at ordinary temperatures, and do not leave a permanent stain on paper. The essential oils are generally obtained by distilling with water the portion of the plant in which they occur. The essential oil is carried over with the steam, and separates from the water which is condensed in the receiver. A familiar and characteristic example of an essential oil is found in **oil of cloves,** a volatile liquid of well-known odor.

Exp. 115. — Into a glass retort of about 250 c. c. capacity, put 5 grms. of whole cloves, and 150 c. c. of water. Insert the neck of the retort loosely into a receiver or flask, kept cool as directed in Exp. 9, § 31. Bring the water in the retort to boiling, and boil until one-half of the liquid has distilled over. The water which condenses in the receiver will be rendered turbid by the "oil of cloves," which has been carried over by the steam, and on standing, the oil, being heavier than water, will collect in drops in the bottom of the receiver.

Fig. 60.



The oil possesses the characteristic odor of cloves, which it also communicates to the water with which it is in contact. The water may be poured off, and the volatility of the oil illustrated by dipping a piece of filter-paper into it, and hanging the paper in the neighborhood of a gas-flame.

The water, which, from its condensation with the oil of cloves, acquires the same odor, is an example of the fragrant "distilled waters" of the apothecaries.

251. **Oil of Turpentine** ($C_{10}H_{16}$). — When incisions are made into the trunks of certain species of pine, there exudes from the wounds a thick resinous substance known as **turpentine.** When ordinary turpentine is distilled with water, there comes over, mixed with the steam, the vapor of an oily liquid, which condenses in the receiver and rises to the top of the condensed water. It is **oil of turpentine**: the residue in the retort is common rosin.

Exp. 116. — Into a glass retort of about 250 c. c. capacity, put 40 grms. of crude turpentine, and 200 c. c. of water. Boil the liquid in the retort, and condense the vapor which is given off, as in Exp. 115. Drops of an oily liquid will rise to the top of the water in the receiver, and form a layer on its surface: it is oil of turpentine.

In this experiment the pitch of northern pines or of the spruce, etc., may be used instead of the "crude turpentine."

252. **Oil of turpentine** is a volatile liquid, and may be distilled unchanged. It will not mix with water, but dissolves freely in alcohol. It is very inflammable, and burns with a smoky flame, as was shown in **Exp. 67, § 181.**

Exp. 117. — Into a small bottle half filled with water, pour a teaspoonful of oil of turpentine, and shake the bottle. The liquid is rendered turbid by the drops of oil scattered through it, but these drops soon collect together, forming a layer on the top of the water.

Exp. 118. — Into a small bottle half filled with alcohol, pour a teaspoonful of oil of turpentine, and shake the bottle. The oil of turpentine dissolves, and a clear homogeneous liquid results.

253. Oil of turpentine is chiefly valuable for its solvent powers. It dissolves the various resins, and is used in the preparation of varnish: it also dissolves sulphur and phosphorus with readiness, and is one of the best solvents of caoutchouc.

254. The essential oils find extensive application in perfumery: they are, however, often replaced by substitutes artificially prepared. Thus for oil of bitter almonds is sometimes substituted nitrobenzol (§ **268**), and, as has already been stated, (§ **233**), various compound ethers, made from fusel oil and other alcohols, are prepared on a very large scale for the confectioner and perfumer.

255. Oil of turpentine is a hydrocarbon of the composition $C_{10}H_{16}$: an isomeric (§ 240) compound also occurs in the various essential oils, such as the oils of bergamot, birch, cloves, caraway, lemons etc. : most of them contain, in addition, a distinctive compound of carbon, hydrogen and oxygen. Certain of the essential oils contain sulphur : thus the essential oils of garlic, onions and assafœtida have the composition $(C_3H_5)_2S$. This compound is the sulphide of the radical **allyl** (C_3H_5). The pungency of the horse-radish is due to a sulphocyanide of the same radical.

It will be noticed that the radical allyl has the same formula as that assigned to glyceryl (§ 241). It is, however, merely isomeric with glyceryl, for the latter replaces three atoms of hydrogen, i. e., is trivalent, while allyl is univalent.

256. **Camphor** $(C_{10}H_{16}O)$. — Among the essential oils, is classed ordinary camphor. It is obtained by distilling with water the wood of a variety of East Indian laurel. At ordinary temperatures, it is a white solid, which, like ice (§ **22**), volatilizes or evaporates without first melting ; it may readily be distilled, or sublimed unchanged. Camphor takes fire at a low temperature and burns with a very smoky flame ; it is only slightly soluble in water, but dissolves readily in alcohol.

Exp. 119. — Into a tall, narrow beaker of about 50 c. c. capacity put 2 or 3 grammes of camphor. Roll up a piece of rather stiff paper so as to form a long conical cap which will fit into the top of the beaker. Place the beaker thus prepared in a sand-bath and heat it ; the camphor soon melts and begins to boil, and the vapor of camphor is condensed on the upper part of the beaker and on the sides of the paper cone in delicate, snow-like crystals or as a crystalline solid.

Exp. 120. — Throw a portion of the sublimed camphor of the preceding experiment into a dish of *clean* water. The camphor will slowly dissolve with a peculiar gyratory motion. Throw another portion into a small quantity of alcohol ; the camphor rapidly dissolves. Place a third portion on a brick and touch it with a lighted match : the camphor takes fire and burns with a smoky flame.

257. Camphor is a compound containing oxygen : other oxygenated essential oils are the oil of bitter almonds, oil of cinnamon and oil of wintergreen : some of these oils will be studied in the succeeding chapter.

The essential oils which have just been studied have no immediate relation to the marsh-gas series of hydrocarbons, which, with the derived compounds, has formed the main subject of this chapter. They are, however, conveniently studied in connection with the fats and fixed oils.

CHAPTER XVI.

CARBON (continued).

258. In the series of **hydrocarbons** known as the **marsh-gas** series, and described in the last chapter, there is a constant difference of CH_2 in the formulæ of succeeding members of the series. There is also a difference of about **30°** between the boiling-points of successive members; and other physical properties, if studied, would show a corresponding and regular increase or decrease. Such series are called **homologous series** (having the same proportion), and the members of the series are **homologues** of each other. For every such series a general algebraic symbol can be devised which will apply to each member of the series. Thus the general formula of the **homologues** of marsh-gas is C_nH_{2n+2}; if $n = 1$, the formula becomes CH_4, marsh-gas; if $n = 3$, the formula becomes C_3H_8, propyl hydride, and so on.

Another series of homologous hydrocarbons is that whose general formula is C_nH_{2n}: the first member of this series is **olefiant gas** (C_2H_4). Members of this series occur among the products of the distillation of various organic compounds, and also in petroleum.

259. **Olefiant gas or Ethylene** (C_2H_4) is a colorless gas, somewhat soluble in water. It occurs among the products of the distillation of bituminous coal, but is best prepared by the action of sulphuric acid on alcohol.

In a flask of at least 750 c. c. capacity mix cautiously, with constant agitation, 120 c. c. of oil of vitriol and 30 c. c. of alcohol. Connect the flask when cool with a delivery-tube dipping into the water-pan, and apply a gentle heat. The colorless gas evolved from the mixture may be collected over water in the usual manner. The mass in the flask blackens, and towards the end of the operation froths considerably, so as to require constant watching. The gas burns with a white flame, as may be shown by applying a lighted match to the mouth of a bottle of the gas, and forcing the gas out by pouring water into the bottle.

Fig. 61.

The reaction which takes place consists in the removal of the elements of water from the alcohol: $C_2H_6O - H_2O = C_2H_4$. Other reactions, however, take place, as the gas prepared in this manner always carries with it some vapor of ether and undecomposed alcohol, together with carbonic acid (CO_2) and sulphurous acid (SO_2).

260. The name **olefiant gas** is derived from the fact, that, when it is brought into contact with chlorine, the two gases unite directly to form an oily liquid, **ethylene chloride, $C_2H_4Cl_2$,** called also **Dutch liquid.**

The formation of ethylene chloride may be shown as follows: Fill a bottle of 500 c. c. capacity with chlorine gas, and pass this gas under water into a bottle of 1000 c. c. capacity, which has been previously half filled with olefiant gas. The mixture of gases thus formed will speedily decrease in bulk, and drops of an oily liquid, ethylene chloride, will collect on the surface of the liquid and sink through the water into the pan, where they may be collected in a porcelain capsule placed under the mouth of the bottle.

If the ethylene chloride thus formed be purified by being shaken up in a bottle containing a solution of sodium carbonate, and then poured out upon a plate, it will be found to possess an agreeable odor something like chloroform.

261. **Ethylene** is the first of a series of hydrocarbons con-

taining one less atom of hydrogen than the corresponding radicals of the **marsh-gas** series. Thus: —

Ethylene	is C_2H_4	while	**Ethyl**	is	C_2H_5
Propylene	" C_3H_6	"	**Propyl**	"	C_3H_7
Butylene	" C_4H_8	"	**Butyl**	"	C_4H_9
Etc.			**Etc.**		

The members of this series act as **bivalent radicals**; they differ in formula from the corresponding alcohols of the marsh-gas series by H_2O, and some of them, like ethylene, can be obtained by distilling the corresponding alcohols with zinc chloride, or, in some cases, with sulphuric acid. Many chemists prefer the terms ethene, propene, butene, etc., to the somewhat longer names here used.

262. **Glycols.** — The members of this series, acting as bivalent radicals, enter into a variety of compounds; one of these compounds, **ethylene chloride** ($C_2H_4Cl_2$), has already been mentioned (§ 260). Bearing the same relation to these radicals that the alcohols (§ 229) do to the radicals of the marsh-gas series is a class of bodies commonly known as **glycols**: thus the formula of **ethylene glycol** is $\left.\begin{matrix}C_2H_4\\H_2\end{matrix}\right\}O_2$. These compounds are also sometimes included in the general term **alcohol**, which is thus seen to have a wider application than that given in § 229. In fact, the term **alcohol**, in its most extended sense, is applied to any organic compound built upon the type of one or more molecules of water in which the radical that replaces the hydrogen contains only carbon and hydrogen. When this radical is bivalent, and replaces H_2 in the type $\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2$, as in **glycol** $\left.\begin{matrix}(C_2H_4)\\H_2\end{matrix}\right\}O_2$, the alcohol is called **diatomic**; when a trivalent radical replaces H_3 in $\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3$, the alcohol is **triatomic**; according to this view, **glycerin**, a compound already studied (§ 241), is regarded as a **triatomic alcohol**.

263. The members of the olefiant-gas series afford an illustration of the value to chemical theory of the determination of the vapor density of compound bodies, — a determination which is a purely physical operation. It will be seen that in each of these hydrocarbons there are two atoms of hydrogen for one atom of carbon, or two parts by weight of hydrogen for twelve parts of carbon. By analysis merely, the formula of these compounds could not be established. As an example, take butylene (C_4H_8): analysis would only show

that six parts by weight of carbon were combined with one part by weight of hydrogen ; a determination of the specific gravity would show the specific gravity of the gas referred to hydrogen to be about 28, and, as has been shown in § 139, the specific gravity of a compound in the state of vapor is one-half its molecular weight. If, then, 28 be multiplied by two, the result will be 56 for the weight of the molecule, and the formula could not be C_2H_4, or C_3H_6, or anything, in short, except C_4H_8. Another help in fixing the place of any member of a given series, if that member be a liquid at the ordinary temperature, is the determination of the boiling-point ; for it has been found that in these various series the boiling-points of successive members increase in a nearly constant ratio.

264. **Phenyl Series** (C_nH_{2n-6}). — If the liquid and semi-liquid products of the distillation of bituminous coal, which collectively are known as **coal-tar,** be subjected to distillation, there will come off, — first, a watery liquid containing ammonium salts ; next, a quantity (amounting to from 5 to 10 per cent of the tar employed) of oil lighter than water, and technically known as **light-oil,** or, when purified, as **coal-tar naphtha ;** if the distillation be carried further, there will come off about 30 per cent of a heavy oil, called **dead oil ;** the residue in the retort, which becomes solid on cooling, is known as **pitch** or artificial asphaltum.

The **light oil** mentioned above consists principally of a mixture of several hydrocarbons of the general formula C_nH_{2n-6}, known as the **phenyl series.** The members of this series, at present of most importance in the arts, are **benzol** (C_6H_6) and **toluol** (C_7H_8) ; from these compounds are derived, by chemical processes, the beautiful and varied coloring matters known as **aniline dyes.** While coal-tar is the chief industrial source of the hydrocarbons of the phenyl series, they have been obtained in less amount from other sources : the petroleum from Rangoon, in the kingdom of Burmah, contains members of this series in small quantity.

265. **Benzol** (C_6H_6) at the ordinary temperature is a mobile, colorless, volatile liquid, crystallizing at 0° : its vapor is very inflammable, and burns with a smoky flame. The illuminat-

ing power of ordinary coal-gas is probably due in considerable measure to the vapor of benzol and its homologues. Benzol is valuable as a solvent, as it readily dissolves sulphur, phosphorus, caoutchouc and other substances. Benzol also dissolves wax and fatty bodies, and is used to remove grease-spots from articles of silk and woollen.

Exp. 121. — Into a small bottle containing several teaspoonfuls of benzol, put a bit of tallow ; close the bottle and shake it : the fat is completely dissolved.

Exp. 122. — Put some of the purest benzol that can be obtained into a test-tube and immerse the tube in a mixture of salt and pounded ice or snow : the benzol will, if pure, become solid; if not pure the benzol will separate from the rest of the liquid in crystals, provided the percentage of other bodies (toluol, etc.) be not too large.

If air be passed through benzol or naphtha, it becomes charged with inflammable vapor, and may then be burned like ordinary coal-gas. Gas-machines constructed on this principle have been in use for some years : latterly, however, benzol and coal-tar naphtha, which were formerly used in them, have been supplanted for such purposes by several cheaper and lighter hydrocarbons obtained from petroleum. The "benzine" now sold for removing grease is usually not benzol, but a mixture of some of the most volatile (and most inflammable) of the compounds obtained from petroleum.

266. **Benzol** (C_6H_6) may be regarded as the hydride of a radical, C_6H_5, called phenyl. Benzol would thus be called phenyl hydride, and the formula written C_6H_5, H. The name benzol is derived from the fact, that this substance can be obtained by the distillation under proper conditions of **benzoic acid,** — a substance which occurs in nature in *gum benzoin.*

267. **Toluol** (C_7H_8) resembles benzol in its chemical characters, and takes part in similar reactions. It may be regarded as methyl-phenyl hydride ($C_6H_4(CH_3), H$) i. e., phenyl hydride, in which one atom of hydrogen has been replaced by the radical methyl (CH_3).

268. **Nitrobenzol** ($C_6H_5(NO_2)$). — By the action of nitric acid on benzol an interesting compound known as **nitro-benzol** is produced.

Exp. 123. — Into a small flask put a teaspoonful of *fuming* nitric acid. Add a few drops of benzol, and warm the mixture *very gently*

over the lamp. Chemical action takes place, and, upon subsequent dilution of the acid mixture with water, a heavy, oily liquid separates.

Nitrobenzol is a heavy, oily liquid insoluble in water, but soluble in alcohol and ether. It has an odor resembling that of bitter almonds, and is somewhat used in perfumery.

Nitrobenzol is interesting, as affording another example of a substitution compound in which the group of atoms NO_2 takes the place of hydrogen (compare nitro-glycerin, § 245): it is, however, chiefly interesting from the fact that it is one step in the process of making **aniline** from benzol.

269. **Aniline** (C_6H_7N) is a volatile, oily liquid somewhat soluble in water, and readily dissolved by alcohol or ether. When pure, it is colorless, but on exposure to air it becomes of a reddish-brown color. A characteristic reaction of aniline is afforded by its deportment to "chloride of lime."

Exp. 124. — Stir up a teaspoonful of "chloride of lime" (bleaching powder) in five times its bulk of water, and filter the solution. Dissolve a drop of aniline in a teaspoonful of water, and add a few drops of this solution to a portion of the solution of bleaching powder. A beautiful purple coloration turning to a dirty red will form in the liquid.

270. **Aniline** may be obtained pure by distilling indigo with caustic potash: it also occurs in very small quantity among the products of the distillation of coal, in the heavy oil of coal-tar (§ **264**); on a large scale, however, it is made from nitrobenzol by the action of *reducing agents* (§ **129**). The formation of aniline from nitrobenzol may be illustrated by the following experiment.

Exp. 125. — Into a wide test-tube put two drops of nitrobenzol and a few small fragments of zinc. Add half a teaspoonful of strong chlorhydric acid. Violent evolution of hydrogen takes place, and the nitrobenzol, which at first is visible in oily globules at the surface of the effervescing liquid, gradually disappears, being converted into aniline, which dissolves in the acid. More zinc or more acid may be added until this result is reached, but the zinc should be in excess. When the nitrobenzol has disappeared and the action of the acid has ceased, dilute a portion of the liquid with an equal bulk

of water and add a drop or two of the bleaching-powder solution, used in Exp. 124. The characteristic purple color produced by the action of bleaching powder upon *aniline* appears in the liquid.

The formula of aniline is C_6H_7N, and it may be regarded as benzol, in which one atom of hydrogen has been replaced by the radical (NH_2) and written $C_6H_5 . NH_2$; or it may be regarded as ammonia (NH_3), in which one atom of hydrogen has been replaced by phenyl (C_6H_5) and written $\left.\begin{matrix} C_6H_5 \\ H \\ H \end{matrix}\right\} N$. Compounds of the ammonia type where a metallic element, or radical acting as a metallic element, replaces one or more atoms of hydrogen, are called **amines**; thus aniline would be called **phenyl-amine**. When in the ammonia type a non-metallic element, or radical acting as a non-metallic element, replaces one or more atoms of hydrogen, the compound is sometimes called an **amide**; as **acetamide**, $\left.\begin{matrix} (C_2H_3O) \\ H \\ H \end{matrix}\right\} N$, where an atom of hydrogen is replaced by the hypothetical radical **acetyl**, C_2H_3O.

271. **Aniline** resembles **ammonia** in its conduct towards acids, uniting directly with them to form salts; thus with chlorhydric acid (HCl) it unites to form a compound C_6H_7N,HCl, or C_6H_8N,Cl, corresponding to ammonium chloride and called "chlorhydrate of aniline," or, better, **phenylium** or **phenyl-ammonium chloride.**

Exp. 126. — Pour a few drops of aniline into a porcelain dish, and hold over the dish a rod which has been dipped in strong chlorhydric acid. White fumes of phenylium chloride are produced. This experiment illustrates both the volatility, and the basic character of aniline.

272. The term *base* has already been defined in §§ 61 and 63. In addition to the applications there mentioned, the term is also used to denote bodies which, like ammonia, NH_3, and aniline, C_6H_7N, contain no oxygen but unite directly with *acids* to form *salts.*

273. **Aniline Colors.** — Aniline itself and the salts of aniline are colorless when pure, but by exposure to the air they become more or less colored. By the action of various chemical agents on aniline, a great number of coloring matters may be obtained.

Red, yellow, green, blue and black, and that, too, in very great variety and beauty of shade, are thus by difference in the chemical treatment, all obtained from the same raw material; namely, coal-tar, a waste product which formerly was of very little value. The intensity of some of these coloring matters is very striking.

Exp. 127. — Take a crystal of aniline red no larger than the head of a pin, dissolve it in a small quantity of alcohol, and then dilute the solution in a clear bottle or in a white porcelain dish with a litre or more of water. The red tint communicated to this large quantity of water will be very perceptible.

274. The various so-called **aniline dyes** are obtained, not from the pure aniline, but from a mixture of aniline and toluidine. **Toluidine** is a body obtained from **toluol** (C_7H_8) by precisely the same steps as are taken in the production of aniline from benzol. Pure aniline alone will not yield the coloring matters.

The chemical agents employed in the production of the aniline dyes are in their general character of an oxidizing nature. The effect of oxidation on the salts of aniline may be shown as follows: —

Immerse the poles of a galvanic battery in an aqueous solution of aniline acidulated with sulphuric acid. At the pole where oxygen is evolved, the solution becomes of a bright red color. In Exps. 124, 125, the "chloride of lime" acted as an oxidizing agent, although the color there produced has little permanence.

The various coloring matters themselves are salts of several compound bodies which bear a certain resemblance to aniline, in that they possess a basic character, that they may be regarded as formed like aniline on the ammonia type, and that they of themselves are colorless: thus the beautiful and much-prized color known as *magenta* is the salt (chloride or acetate) of a compound called rosaniline. This salt occurs in commerce finely crystallized; the crystals are of a brilliant green metallic color by reflected light, while by transmitted light they appear of an intensely red color.

275. **Phenic** or **Carbolic Acid** (C_6H_6O). — Somewhat closely related to the phenyl series of hydrocarbons is a body which

occurs in the oil distilled from coal-tar, and is known as **phenic** or **carbolic acid.** The pure acid crystallizes in colorless needles, which liquefy in moist air, and are sparingly soluble in water. Phenic acid has an odor like wood-smoke, and possesses powerful antiseptic properties. Phenic acid is used, as are also certain of its salts (**phenates** or **carbolates**), to prevent the spread of infectious diseases, and in the treatment of sores which give offensive discharges: it is also used in the preparation of a variety of "disinfecting" and "purifying" powders, and of "carbolic acid soap" used for similar purposes. The **dead oil** of coal-tar, which is used as a preservative of timber, probably owes its antiseptic properties, in part at least, to the carbolic acid which it contains.

Exp. 128. — Dissolve 1 grm. of crystallized carbolic acid in 100 c. c. of water, and in the solution thus prepared soak a piece of fresh meat, or a small fish, for one hour, and then hang the meat or fish up to dry. The animal matter thus preserved may be kept almost indefinitely in a dry place without undergoing putrefaction.

Carbolic acid possesses only weak acid properties. If its symbol be written C_6H_5,HO it is seen to bear the same relation to the radical phenyl that the alcohols do to the radicals of the marsh-gas series. It is commonly called phenol by chemists, and is one of a class of similar compounds called **phenols.**

276. The dead oil of coal-tar contains several other acid bodies analogous to carbolic acid: it also contains several bases, among which is aniline (§ **270**), and several hydrocarbons, among which may be mentioned naphthalin (§ **279**), and anthracene (§ **281**).

277. **Trinitrophenic** or **Picric Acid.** — When phenic acid is treated with strong nitric acid, a compound known as **picric acid** is produced. It is a substance which forms yellow crystals not very soluble in water, but possessing great coloring power. It is readily soluble in alcohol and ether, and is used principally in dyeing silk. Picric acid may be formed by the action of nitric acid on various other organic compounds, especially on certain gum resins; on the large scale, however, it is manufactured from phenic or carbolic acid.

Exp. 129. — Into a flask of 150 c. c. capacity, put two teaspoonfuls of fuming nitric acid. Add cautiously and very gradually, half a teaspoonful of crystallized carbolic acid or of the liquefied crystals. The action which takes place is very violent, and nitrous fumes are copiously disengaged. When the action has subsided allow the flask to become cold ; yellow crystals of picric acid will be found in the liquid.

This experiment should be performed where there is a good draught of air, and the flask should be held at arms' length on each successive addition of carbolic acid.

Exp. 130. — Dissolve 1 grm. of crystallized picric acid, in 125 c. c. of water. Preserve one-half the solution for use in a subsequent experiment ; warm the remainder gently, and immerse in it some woollen material, — a skein of white yarn, or piece of white flannel. After a few minutes, remove the wool, and rinse it in water : it will be dyed a brilliant yellow.

The formula of picric acid is $C_6H_3(NO_2)_3O$, or phenic acid, C_6H_6O, in which three atoms of hydrogen are replaced by three atoms of the radical NO_2 ; hence the chemical name, **tri-nitrophenic acid**.

278. **Picric acid** is used in the preparation of potassium picrate, which is an ingredient of certain substitutes for gunpowder. The **picrates** are yellow crystalline salts. When heated, they are decomposed with explosion : picric acid itself explodes if heated suddenly, although with care it can be gradually sublimed. Potassium picrate will explode, if struck with a hammer.

279. **Naphthalin** ($C_{10}H_8$). — This hydrocarbon is an abundant product of the distillation of coal-tar, occurring especially in the dead oil, and in largest amount towards the last part of the distillation. It is solid at ordinary temperatures, and is separated from the accompanying liquid products by pressure. It is insoluble in water, but dissolves in alcohol, and may be purified by recrystallization from this solvent. It can also be sublimed unchanged. It forms white pearly crystals greasy to the touch : it is not readily inflammable, but, when lighted, burns with a smoky flame.

280. Naphthalin enters into direct combination with chlorine and

bromine in different proportions: it also forms, with these elements, a great number of **substitution compounds**, as they are called. These compounds preserve the type of naphthalin, but in them one or more atoms of chlorine or bromine, or both these elements, take the place of the same number of atoms of hydrogen. One of these compounds furnishes a good example of **isomerism**, defined in § 240. Of the compound whose formula is $C_{10}H_6Cl_2$, there have been recognized seven distinct varieties; that is, there are seven compounds which have identically the same percentage composition, and to each of which the formula $C_{10}H_6Cl_2$ will apply, but which differ from each other in respect to solubility, fusing point and behavior to chemical agents. These differences may be imagined to be due to diversities in the arrangement of the atoms in the several compounds.

281. **Anthracene** ($C_{14}H_{10}$) is a white solid, which accompanies naphthalin in the last products of the distillation of coal-tar. It is insoluble in alcohol, and may be separated from naphthalin by treating the mixture of these two substances with this solvent, which removes the naphthalin. It is interesting chiefly because from it **alizarin**, a coloring matter formerly obtained from the madder-root, is now made in large quantities.

282. **Destructive Distillation of Wood.** — In the distillation of wood, as in that of coal, the nature of the products varies somewhat according to the temperature employed. The gas obtained consists mainly of carbon protoxide, carbonic acid, marsh-gas and hydrogen; of the liquid and semi-liquid products, a portion is insoluble in water and is composed of various hydrocarbons, some of which have already been studied. Of the portion soluble in water, the most important constituents are **wood-spirit** (methyl alcohol, § **230**), **methyl acetate** and **acetic** or **pyroligneous acid** (§ **238**).

The greatest yield of acetic acid is obtained by distilling the wood at low temperatures. The liquid portion, insoluble in water, contains among other bodies, some of the homologues of benzol, and a body called **kreasote**, which, when pure, is a colorless liquid of pungent taste and smoky odor. The peculiar odor of wood-smoke is owing to the presence of this body.

Kreasote possesses very powerful antiseptic properties: meat and fish may be preserved from putrefaction by immersion in a very dilute solution of kreasote, or by exposure to wood-smoke. Much of what is now sold as kreasote is actually **carbolic acid**, which, as has been seen in **Exp. 128**, possesses marked antiseptic properties.

Paraffin ($C_{27}H_{56}$?) is also among the products of the distillation of wood; but the paraffin of commerce is now obtained almost entirely from petroleum.

In § **257**, among the essential oils, was mentioned the **oil of bitter almonds.** This substance is closely allied with the phenyl series of hydrocarbons, and may be most conveniently studied at this point.

283. **Oil of Bitter Almonds.** — If the kernels of the bitter almond be crushed, there is expressed a nearly colorless fixed oil without taste or odor, and identical with that obtained from the sweet almond. If, however, the crushed kernels are moistened with water, the familiar odor of bitter almonds is soon developed. Bitter almonds contain a peculiar nitrogenous substance, **amygdalin** ($C_{20}H_{27}NO_{11}, 3\,H_2O$); under the influence of another nitrogenous body, contained in the kernels and resembling somewhat the **diastase** of malt (§ **300**), the amygdalin is converted into an essential oil, the **essence** or **oil of bitter almonds.** There is formed at the same time a quantity of **cyanhydric acid** (§ **212**), which accompanies the essence when it is distilled, and communicates to it its highly poisonous qualities. The purified oil is not poisonous.

284. The formula of the oil of bitter almonds is C_7H_6O, and it may be regarded as a hydride of a hypothetical radical **benzoyl** (C_7H_5O). The relation of the oil of bitter almonds to the phenyl series (§ 264) is seen by regarding it as an **aldehyde** bearing the same relation to toluol, C_7H_8, (§ 267), that ordinary aldehyde (§ 235) does to ethyl hydride, C_2H_6. It behaves like an aldehyde: in contact with the air, it oxidizes to **benzoic acid** ($C_7H_6O_2$), which, to carry out the same comparison, answers to acetic acid. There is also a compound which corresponds to alcohol, **benzyl alcohol** (C_7H_8O).

The relations of these compounds to each other are shown in the following table : —

Radical. — Ethyl. C_2H_5	**Ether.** — Ethyl ether. $(C_2H_5)_2O$
Methyl-phenyl or *benzyl*. C_7H_7	Benzyl ether. $(C_7H_7)_2O$
Hydride. — Ethyl hydride. $(C_2H_5)H$	**Aldehyde.** — Acetic aldehyde. C_2H_3O,H
Toluol or benzyl hydride. C_7H_7,H	Bitter almond oil. C_7H_5O,H
Alcohol. — Ethyl alcohol. C_2H_5,HO	**Acid.** — Acetic acid. C_2H_3O,HO
Benzyl alcohol. C_7H_7,HO	Benzoic acid. C_7H_5O,HO

285. **Benzoic acid** ($C_7H_6O_2$) occurs in many balsams, being found most abundantly in gum benzoin, a sort of balsam containing besides benzoic acid several resins. It may be prepared artificially from bitter almonds, as has been stated ; it may also be prepared by oxidizing naphthalin with nitric acid, and heating the product with slaked lime. Calcium benzoate is thus produced, from which benzoic acid may be set free. Benzoic acid is a white crystalline solid, of pearly lustre.

If benzoic acid be distilled with excess of lime, benzol is produced in accordance with the equation : —

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} = \underset{\text{Benzol.}}{C_6H_6} + \underset{\text{Calcium carbonate.}}{CaCO_3}.$$

286. **The Acetylene Series** (C_nH_{2n-2}). — **Acetylene** (C_2H_2) is a transparent, colorless gas, which occurs in small quantities in illuminating gas. It may be formed by the direct union of carbon and hydrogen at very high temperatures. It is also formed during the incomplete combustion of other hydrocarbons. The peculiar odor noticed when the gas in a Bunsen lamp burns at the lower opening is due to the formation of acetylene. Acetylene burns with a bright flame, and as it is present to some extent in coal-gas, it doubtless contributes to the illuminating effect of the gas.

CHAPTER XVII.

CARBON (continued).

287. In this chapter several of the natural organic compounds will be considered which play a part in the life and growth of plants and animals, or are the direct product of such growth. A great number of different compounds occur in the vegetable kingdom, some being found only in particular species of plants, or even being confined to single portions of particular plants, while others occur almost universally in nearly all vegetable organisms. Among these substances which occur so widely diffused are **water,** which sometimes amounts to 90 per cent of the green plant, **woody fibre** or **cellulose, gum, starch** and **sugar.** The last-named compound will first claim our attention.

The class of bodies known as **sugars** contains several varieties, of which the most familiar is ordinary **cane-sugar.**

288. **Cane-Sugar** or **Sucrose** ($C_{12}H_{22}O_{11}$) occurs in the juice of various plants, notably in that of the sugar-cane, beet-root, sugar-maple and certain varieties of palm. In this country sugar made from the cane is used almost exclusively, but on the continent of Europe large quantities are made from the beet-root.

289. **Sugar Manufacture.**—In the manufacture of cane-sugar, the juice is extracted from the canes by passing them between grooved iron cylinders. The liquid thus extracted contains not only sugar in solution, but also certain albuminous and waxy matters, and has a great tendency to ferment. It is therefore immediately treated with a small proportion of milk of lime and heated for a short time. The lime serves to correct any acidity and at the same time enters into combination with some of the impurities of the juice; the albuminous matters, coagulated by the heat, entangle these impurities and rise with them as a thick scum to the surface of the liquid. The scum is removed, and the clear liquid is evaporated in open pans until of such a consistency that on cooling crystals of sugar separate. The

crystals, after draining, form what is known as *brown* sugar; the mother-liquor which drains off is molasses.

Until recently almost all the sugar manufactured was exported from the place of its production as "brown" or "muscovado" sugar, and was subsequently refined in England or in the more Northern cities of the United States. The *refining* consists in dissolving the sugar in water, removing the impurities and coloring matters by filtering the liquor, and passing it through layers of animal charcoal, and then evaporating and crystallizing. The evaporation is conducted in a peculiar manner. If a solution containing a certain amount of common salt be evaporated, the salt is recovered unchanged, no matter how rapidly or how slowly the evaporation takes place; this is not the case with sugar. If a solution of cane-sugar be boiled, a certain amount of the sugar undergoes a change: it is converted into another variety of sugar, or rather a mixture of two varieties of sugar. These varieties of sugar (which will be considered hereafter) do not crystallize out with the cane-sugar, but form the main part of the sirup which drains off from the crystals. The amount of sugar which is thus changed depends among other things upon the length of time during which the solution is boiled, and also upon the temperature employed. By boiling in open pans, much sugar is thus lost; and in the sugar refineries the sugar is therefore boiled in enormous closed iron or copper kettles, from which the air can be exhausted. Under these circumstances the sugar solution boils at a much lower temperature than it would in the open air, and all risk of burning is avoided. When a sufficient degree of concentration is reached, the liquor is removed from the "vacuum-pan," as the kettle is called, and allowed to crystallize. The crystals are dried either by allowing them to drain in moulds (loaf-sugar), or by forcing the mother-liquor out by means of a centrifugal machine (granulated sugar). When, by further concentration of the liquor which drains off, and by repeated crystallizations, the greater part of the sugar has been obtained, the mother-liquor remaining from the last crop of crystals is sold as sirup. Until within a few years, almost all the refining of sugar was done in England and the Northern United States, and enormous quantities of sugar are still refined in these countries; of late years, however, vacuum-pans and other improved apparatus have been introduced into the places where sugar is produced, and very good white sugar is there made directly from the juice of the cane. The following experiment will illustrate the principle of the vacuum-pan alluded to above.

Exp. 131. — Fill a round-bottomed flask of 500 c. c. capacity half full of water, and boil it over the lamp. When the boiling has continued for some time, and the air in the upper part of the flask has been expelled by the steam, remove the lamp, grasp the neck of the flask with a dry warm towel and immediately insert a tightly fitting cork. Support the flask in an inverted position and pour cold water over the bottom, which is now uppermost, so as to condense the steam; there will be formed a vacuum above the water and boiling will recommence. This may be repeated several times, until the water has cooled down to a considerable extent.

290. The process of the manufacture of sugar from the beet is very similar to that already described. A comparatively small quantity of sugar is made in the Northern United States by concentrating the sap of the sugar-maple, and in the East quite considerable quantities are made from the juice of several varieties of palm, especially the date-palm.

The sugar obtained from all these sources is identical with that obtained from the sugar-cane. Care is, however, required in the purification in order to remove completely a peculiar taste which betrays the origin of the sugar. Maple-sugar and palm-sugar are sold in the crude state, the peculiar taste being agreeable to many persons; beet-sugar is always refined, as the taste of the crude article is offensive to every one.

Exp. 132. — Stop the neck of a funnel loosely with a bit of pumice-stone and fill it nearly to the top with common maple-sugar, which has been reduced to a rather fine powder. Prepare a saturated solution of sugar by dissolving 50 grms. of white sugar in 20 c. c. of hot water, and allowing the solution to cool. Pour some of this solution upon the maple-sugar as it lies in the funnel, so as to make a layer 0.5 c. m. thick: support the funnel in a small bottle, cover it with a sheet of paper, and let it remain for some time. The solution of sugar will gradually work its way through the maple-sugar, and being already saturated, it will not dissolve any of it; it will, however, carry with it a considerable quantity of the coloring matter and when the maple-sugar has drained, it will be much lighter colored than before, and will have lost, to a certain degree, its peculiar taste.

291. **Sucrose** is readily soluble in water, and may be ob-

tained from its solution in large transparent crystals, **rock-candy.** Sucrose melts at 160° to a colorless liquid, which on cooling forms a transparent amber-colored mass, **barley-sugar.** When sucrose is heated to 215°, water is given off, and a brown mass, **caramel,** remains.

Exp. 133. — Heat *cautiously* a small quantity of white sugar in a porcelain dish until it melts. Allow the pasty liquid to cool rapidly ; the product is **barley-sugar**. Heat again to a still higher, but not too high temperature ; the sugar turns brown, froths, gives off pungent vapors and there remains a dark brown mass, which is **caramel.** This substance is soluble in water, and is used to color soups, ale, wines and so forth. If sugar be heated rapidly and rather strongly, it will take fire and burn, leaving a black carbonaceous residue.

292. When a solution of sucrose is subjected to the action of yeast, the sucrose is converted into two isomeric (see § 240) varieties of sugar, **dextrose** and **levulose**, in accordance with the equation :

$$\underset{\text{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}.$$

The same change may be effected by simply boiling the solution of sucrose for a long time ; it may be effected more rapidly by the addition of a small amount of almost any organic acid or of one of the stronger acids, such as sulphuric or chlorhydric. These facts have a practical bearing on the manufacture of sugar ; for, as has been already stated, a considerable amount of cane-sugar is lost, even in the best-conducted processes of extracting it from the juice and refining the crude product.

293. The most striking physical property of sugar is its action upon polarized light. If a beam of polarized light be passed through a solution of cane-sugar, the plane of polarization will be rotated towards the right : the same is true of dextrose, though in a less degree, and hence its name (Latin, *dextra*, the right hand) ; levulose, on the contrary, turns the plane of polarization to the left (Latin, *læva*, the left hand). The amount of rotation in any case depends upon the amount of sugar in the solution examined, and upon this fact methods have been based for the quantitative estimation of cane-sugar in sirups or solution thereof.

294. **Dextrose, Grape-** or **Starch-Sugar** ($C_6H_{12}O_6$), also called **Glucose,** occurs together with sucrose and levulose in many ripe

fruits, such as apricots, peaches, pineapples and strawberries; together with levulose it occurs in honey and in certain fruits, among which are grapes, cherries and gooseberries. The sugar formed in dried fruits, such as raisins, which have *candied*, is grape-sugar. It may also be prepared by boiling starch in water acidulated with sulphuric acid.

Exp. 134. — Into a flask of 250 c. c. capacity, introduce 100 c. c. of water. Add 1 c. c. of strong sulphuric acid, and heat the mixture to boiling. In a porcelain mortar, rub 10 grms. of starch with enough water to make a cream, and pour the mixture, little by little, into the boiling liquid, taking care not to interrupt the boiling. The starch dissolves without forming a paste. Boil for three or four hours, replacing from time to time the water lost by evaporation, and then add powdered chalk (calcium carbonate) until the liquid is no longer acid. When the mixture has become cold, filter off the insoluble calcium sulphate formed by the action of the sulphuric acid on the calcium carbonate, and evaporate the solution at a gentle heat to a sirupy consistency. The solution contains dextrose, which on long standing may separate from the liquid in crystals.

Dextrose may be obtained from cellulose or woody fibre (§ 309), by treating linen or cotton shreds, or even sawdust, with strong sulphuric acid. The mixture is allowed to stand for 24 hours, and then diluted with a large quantity of water and boiled. The acid is subsequently neutralized with chalk, and the dextrose obtained, as in Exp. 134. In these experiments, the sulphuric acid acts in some unexplained manner by its simple presence. When the reaction is completed, there remains in the solution the same amount of sulphuric acid as was added in the beginning of the experiment.

295. **Dextrose** may be obtained in crystals which contain one or two equivalents of water; it usually occurs, however, in the state of a thick solution, as in **Exp. 134**, or as it exists in *sirup*. It is used in the manufacture of **alcohol** (§ **226**), in the sweetening of certain varieties of wine and beer, and is sometimes employed to adulterate cane or beet sugar, especially in confectionery. It possesses less sweetening power than cane-sugar.

296. **Levulose** or **Fruit-Sugar** ($C_6H_{12}O_6$) occurs mixed with

one or both of the preceding varieties of sugar, in honey and in many kinds of fruits. It is formed together with dextrose, when ordinary sugar is boiled, and hence occurs in molasses. It may be made from **inulin**, a variety of starch obtained from the dahlia and some other plants, in the same way in which dextrose was made from common starch (**Exp. 134, § 294**). It does not crystallize : by evaporating its solution, it is obtained as a colorless, amorphous mass.

297. Under the influence of yeast, both dextrose and levulose undergo fermentation, carbonic acid and alcohol being formed. Cane-sugar does not undergo fermentation directly, but is first changed into a mixture of dextrose and levulose.

298. A characteristic test for **dextrose** and **levulose** is afforded by their chemical action on an alkaline solution of a salt of copper.

Exp. 135.—To a dilute solution of copper sulphate, add a little tartaric acid and then enough caustic potash to dissolve any precipitate which forms. To half of the mixed solution add a few drops of a solution of white sugar, and warm the mixture : no change takes place. To another portion add a solution of grape-sugar, and warm the mixture : a yellowish precipitate of a hydrate of copper forms in the liquid, and by the boiling is converted into the red copper suboxide. By means of this test, the presence of dextrose and levulose may be shown in molasses or sirup.

299. **Lactose** or **Milk-Sugar** ($C_{12}H_{22}O_{11}$) is an animal product nearly related to cane-sugar. It is less sweet and less soluble in water than cane-sugar. It occurs in the milk of the mammalia, and is obtained, chiefly in Switzerland, by evaporating the whey of cows' milk : it crystallizes in hard, gritty crystals, which contain one molecule of water of crystallization.

300. **Fermentation.** — As has already been stated in § **225**, and illustrated by **Exp. 100, § 226,** the juice of various fruits, or aqueous solutions of grape-sugar, in the presence of an organized substance known as **yeast,** undergo a change. The sugar is gradually converted into alcohol, while carbonic acid escapes from the liquid. Cane-sugar, as such, does not undergo this

fermentation, but is first converted into a mixture of dextrose and levulose. Lactose, when pure, is not susceptible of fermentation, although milk can be fermented. In this case, there is formed along with the alcohol a quantity of an acid called **lactic acid.**

Fermented Liquors. — Wines. — The various sorts of wines are produced by the spontaneous fermentation of the juice of grapes. No yeast is necessary, as simple exposure to the air causes fermentation to set in (see § 225). Sweet wines are those in which there remains a portion of grape-sugar, which has not been converted into alcohol. Champagne is wine that has been bottled while active fermentation is going on, and contains a considerable amount of carbonic acid in solution.

Ale and Beer. — The seeds of all plants contain a certain proportion of a body known as starch (§ 301). By treatment with very dilute sulphuric acid, starch may be converted into grape-sugar (see Exp. 134, § 294). A similar change takes place in the germinating seed under the influence of a substance called **diastase**, which is developed in the seed. Advantage is taken of this fact in the manufacture of ale and beer.

Ale and beer are generally prepared from barley. The grain is caused to germinate, by placing it under favorable conditions of moisture and temperature. When the germination has reached a certain point, it is checked by drying the grain at a sufficiently high temperature ; the product is now known as **malt**, and the process is termed **malting**. The malt is ground and heated with water for some hours, nearly to the boiling-point. Under the influence of the diastase developed in the grain during the malting, the starch is converted into dextrin and sugar. To the infusion thus obtained, the **wort**, is added the proper amount of yeast, which causes fermentation to set in.

The proportion of alcohol in the various beers and ales varies from 3 to 9 per cent : beer also contains some acetic acid, the various soluble mineral substances of the grain, some unaltered sugar and dextrin, some diastase and coloring matters. The bitter taste is imparted by the addition of hops before fermentation begins. The foaming is caused by free carbonic acid, the peculiar consistency of the foam being apparently due to the presence of dextrin.

Other Fermented Liquors. — The juice of almost all fruits may be fermented with formation of alcoholic liquors : thus cider is the

fermented juice of the apple ; perry is made from pears. From the juice of the currant, gooseberry, blackberry, etc., fermented liquors are obtained popularly called wines. The South Sea islanders ferment the juice of the cocoanut ; the Eastern nations obtain an intoxicating liquor from certain palms.

Distilled Liquors. — Absolute alcohol may be obtained by repeated distillation of any fermented liquor, and final rectification over quicklime (§ 227). When, however, the liquors are simply distilled, there is condensed with the alcohol more or less water, together with certain volatile bodies, which communicate a distinctive flavor to the product. Brandy is obtained by distilling wine : gin is spirit, flavored by distilling it with juniper-berries ; whiskey is prepared by distilling wort made from corn, rye or other grain ; rum was originally made by fermenting molasses, and subjecting the product to distillation.

301. **Starch** ($C_6H_{10}O_5$) is an organized body found in wheat, maize and all other grains, in the tubers of the potato, in the roots and stems, or in the fruits of many other plants. The following experiment will illustrate the manner of obtaining it from the potato, which contains on the average 20 per cent of it.

Exp. 136. — Reduce a clean potato to pulp by scraping or grating ; mix the pulp with water, and squeeze through a linen or cotton cloth, repeating the operation several times. The woody fibre or cellulose, of the potato remains on the cloth while the starch passes through the meshes, and remains suspended in the *filtrate*. Allow the liquid to stand until the starch has settled, then pour off the water, and dry the residue.

302. **Starch** has the appearance of a white powder, but under the microscope it is seen to be made up of distinct rounded or oval grains, which vary somewhat in size and appearance according to the particular plant from which the starch was derived. The grains of potato-starch are about $\frac{1}{300}$ inch in diameter ; those of wheat-starch, $\frac{1}{1000}$ inch ; those of rice-starch are about $\frac{1}{300}$ of an inch. **Fig. 62** represents the grains of potato-starch very much magnified.

303. **Starch** is almost entirely insoluble in water, but when heated in water to about 70°, the granules swell and burst, and

the mixture forms a jelly or paste (**Exp. 39, § 93**) : this starch-paste is used by the laundresses for stiffening linen. A characteristic property of starch is its power of forming a blue color with iodine (**Exp. 39, § 93**). By heating with dilute acid, starch is converted into dextrose (**Exp. 134, § 294**).

Fig. 62.

Inulin is a substance of the same composition as starch : it occurs in the roots of the dahlia, dandelion, chiccory and other plants belonging to the family of *compositæ*. It exists in the plant in a liquid form, it is soluble in hot water, is not colored blue by iodine, and by heating with dilute acids is converted into levulose. **Arrow-root** and **tapioca** are varieties of starch prepared from the roots of tropical plants. **Sago** is the starch obtained from the pith of the sago-palm. The peculiar appearance of tapioca and sago is owing to the manner in which the starch is prepared, and these varieties of starch, or, rather, successful imitations of them, are produced artificially from ordinary starch.

304. **Dextrin.** — When starch is heated to about 205°, it is converted into **dextrin,** a substance of the same chemical composition as starch, but differing in many of its properties. It is soluble in water, forming a gummy solution, and is used, instead of gum-arabic, in the manufacture of adhesive stamps and for other purposes.

Exp. 137. — Heat carefully in a porcelain dish a teaspoonful of powdered starch with constant stirring. It gradually turns brown. After heating for about five or ten minutes, add four times its bulk of water and boil. A solution of dextrin will be obtained, which may be filtered from the unaltered starch. To a portion of the solution add twice its bulk of alcohol ; dextrin will be precipitated, as it is insoluble in alcohol.

305. If starch be heated for some time with water contain-

ing a small amount of sulphuric acid, the starch is converted into dextrin ; if the mixture of starch and water be heated still further, or be actually boiled, the starch (or dextrin) will be converted into starch-sugar (see **Exp. 134, § 294**). This change of starch to dextrin and sugar takes place in nature in germinating seeds by the action of the nitrogenous substance called **diastase** (**§ 300**).

306. **Gluten.** — It has been stated that starch occurs in the different varieties of grain : its presence in wheat, as well as the presence of another body, known as **gluten,** may be shown by the following experiment.

Exp. 138. — Wet a handful of wheat flour with enough water to make a thick dough. Wrap the dough in a linen or cotton cloth, and knead it in a slow stream of water until the water is no longer rendered turbid. The turbidity is caused by particles of starch in suspension ; if a portion of the water be allowed to stand, the starch will be deposited, and may be recognized by means of the iodine test. The tough, viscous mass remaining in the cloth is *gluten.* In addition to these two substances, the wheat flour contains a small amount of sugar and dextrin, which, in this experiment, are dissolved by the water, and a little oil and woody fibre which remain with the gluten.

307. **Bread.** — In the preparation of bread by means of yeast, the flour is made into a dough with water mixed with a certain amount of yeast, and the dough left in a warm place to *rise.* Fermentation sets in : the sugar and a part of the dextrin of the flour are gradually converted into alcohol and carbonic acid, and the latter being set free as a gas causes the dough to swell up and become porous. When the bread is baked, the carbonic acid is expanded still more, and, as it escapes from the bread together with the alcohol, which at the temperature of the oven is converted into vapor, it communicates the desired lightness to the bread. During the process of baking, some water is also expelled from the loaf, and the starch is converted into a gelatinous condition. At the outside of the loaf further decomposition takes place, a substance like caramel being formed which constitutes the *crust.* The crust also contains dextrin, and if the outside of the loaf be moistened and then dried in the oven, the dextrin thus dissolved and left again by evaporation produces a smooth, shining surface.

308. **Cellulose** ($C_{18}H_{30}O_{15}$) occurs in all plants and in all the various parts of the plant. It constitutes the outside of the cells of which every vegetable organism is made up, and occurs in a great variety of forms. The ground-work of succulent fruits, like the apple and pear, of roots like the turnip and beet, as well as of all varieties of trees, even the box and the lignum-vitæ, is cellulose. Linen and cotton are nearly pure cellulose, the fibres themselves being long cells; but in almost all cases the cellulose is accompanied by another substance which incrusts the interior of the cells and predominates in the case of the harder woods and in the shells of the different sorts of nuts. This incrusting substance is of uncertain composition, as it never has been obtained sufficiently pure for analysis. It is much more readily acted upon by chemical agents than cellulose, and by treating woody fibre with acids and alkalies, cellulose may be obtained nearly pure. The finest kinds of filtering (unglazed) paper are nearly pure cellulose. In **Exp. 136** the substance remaining in the cloth was mainly cellulose.

The percentage composition of cellulose is the same as that of starch, dextrin and inulin, and would be most simply expressed by the formula $C_6H_{10}O_5$. It is probable, however, that the true formula of cellulose is some higher multiple of these numbers, not less than $C_{18}H_{30}O_{15}$.

309. Pure **cellulose** is a white substance insoluble in water or alcohol. Strong alkali decomposes it with formation of oxalic acid (§ **322**); strong sulphuric acid dissolves it, and on diluting the solution and boiling, the cellulose is converted first into **dextrin** and finally into **grape-sugar.** By short contact with sulphuric acid of a particular strength, cellulose is converted into a semi-transparent, tough substance resembling animal membrane. Paper thus treated is changed into a substance known as **vegetable parchment.**

Exp. 139. — To 10 c. c. of water in a porcelain dish add slowly, with constant stirring, 25 c. c. of strong sulphuric acid. When the mixture has become perfectly cold, immerse in it a piece of filtering-

paper. Allow the paper to remain in the liquid for 15 or 20 seconds; then remove and rinse thoroughly to remove the acid, first with pure water, then with water containing a little ammonia, and finally with pure water again. The paper is converted into vegetable parchment. If the first experiment be not successful, repeat with fresh pieces of paper, varying the time of immersion until a good result is obtained.

310. By treatment with a mixture of nitric and sulphuric acids, cellulose is converted, without change of form, into a compound called **nitro-cellulose, pyroxylin** or **gun-cotton.** This substance is very explosive, although not nearly as much so as **nitro-glycerin,** which is prepared from glycerin in a similar manner. In the air it burns with a sudden flash without smoke. If burned in a confined space, it produces explosive effects similar to those produced by gunpowder.

Gun-cotton is, chemically speaking, cellulose in which a certain number of atoms of hydrogen are replaced by a corresponding number of atoms of the radical NO_2. Its exact composition differs according to the strength and proportions of the acids used in its formation, there being several distinct varieties.

Collodion is the name given to the solution of a certain variety of pyroxylin in a mixture of alcohol and ether. When this solution is exposed to the air in a thin layer, the solvent rapidly evaporates and leaves a transparent film of pyroxylin. Collodion is much used by photographers.

311. **Gum. — Gum-arabic** is a familiar example of a class of bodies which occur in the juice of almost all plants. Gum-arabic exudes from a species of acacia. It is valuable chiefly on account of forming with water a sticky, mucilaginous liquid.

The **gums** are soluble in water, but insoluble in alcohol, as may be illustrated in the case of gum-arabic by the following experiment.

Exp. 140. — Dissolve 10 grms. of gum-arabic in 75 c. c. of water. The solution is facilitated by powdering the gum-arabic, mixing it with clean dry sand and stirring the mixture from time to time. When solution has been effected, allow the sand to settle and pour off the liquid.

To a portion of the solution thus prepared, add half its bulk of alcohol: the gum is reprecipitated.

312. **Gum-arabic** is a mixture of the calcium and potassium salts of **arabic acid**; calcium and potassium arabates are soluble in water: many other arabates are insoluble in water.

Exp. 141. — To a portion of the solution of gum-arabic of Exp. 140 add an ammoniacal solution of lead acetate (prepared by adding to an aqueous solution of lead acetate ammonia-water in quantity insufficient to produce a precipitate): a white precipitate of an arabate of lead is formed.

To the class of **gums** belong the exudations from trees like the cherry, peach and plum; but the substances which exude from pines and similar trees, often called gum, as *spruce gum*, for example, belong to a different class of bodies, — that of the resins (§ 316).

Gum-tragacanth is a modification of ordinary gum. When treated with water, it swells up, but does not dissolve: 4 or 5 grms. of this gum are sufficient to convert a litre of water into a pasty mass. Similar to gum-tragacanth is *vegetable mucilage*, a substance which occurs in the root of the marsh-mallow, and also in flaxseed and the seeds of the quince.

313. **Pectose.** — In the flesh of unripe fruits, and in such roots as the turnip, beet, carrot, etc., there exists, along with the **cellulose** (§ **308**), a body to which the name of **pectose** has been given. It has as yet been impossible to separate this substance from the cellulose, and its existence has been rather inferred from the products of its transformation than proved by actual isolation. By the ripening of the fruit, or under the influence of heat, acids or other chemical agents, the **pectose** is changed into **pectin**, a substance soluble in water, but insoluble in alcohol.

Exp. 142. — Reduce several white turnips or beets to pulp, by grating. Enclose the pulp in a piece of cotton cloth, and wash by squeezing in water, until all the soluble matters have been removed, or until the water comes off nearly tasteless. To the washed pulp, add enough dilute chlorhydric acid (1 part by measure of the strong acid to 15 parts of water) to saturate the mass, and allow it to stand for 48 hours. At the end of that time, squeeze out the acid liquid, filter it, and add an equal bulk of alcohol. Pectin will separate as a gelatinous, stringy mass.

314. The viscid gummy juice which oozes from baked apples is a strong solution of **pectin.** The various sorts of fruit-jellies are composed of other products of the transformation of **pectose** (pectic and pectosic acids).

Exp. 143. — Stew a handful of sound cranberries covered with water just long enough to make them soft. Observe the speedy solution of the firm pectose. Strain through a cloth. The juice contains dissolved pectin, which may be precipitated by the addition of alcohol to a portion of the juice. Heat the remainder of the juice in a flask on the water-bath (see Appendix, § 17). After a time, which is variable according to the condition of the fruit, and must be ascertained by trial, the juice on cooling or standing solidifies to a jelly that dissolves on warming, and re-appears on cooling; this jelly is **pectosic acid.** By further heating, there may be formed a jelly which is permanent when hot; this jelly is **pectic acid.**

315. **Balsams.** — The term **balsam** is applied to the soft viscid substances which exude from the bark of certain trees, or are obtained in greater quantity by making incisions into the wood of the trees. Canada balsam, balsam of Copaiba, spruce gum and ordinary turpentine are examples of this class of bodies. The **balsams** are complex substances: they consist in the main of an **essential oil** which holds in solution bodies of peculiar character known as **resins.** When the balsams are distilled with water, the essential oil passes over with the steam, and the resin remains behind. This fact has already been illustrated in **Exp. 116,** and in this experiment it was seen that after the distillation there remained in the retort a substance which, although quite fluid at the temperature of boiling water, solidified on cooling to a vitreous semi-transparent mass: it was common **rosin,** a familiar example of the class of **resins.**

316. **Resins.** — The **resins,** as has been stated above, are generally obtained by making incisions in the wood of the trees by which they are produced. From these incisions they exude mixed with the essential oil of the plant. Common rosin, which belongs to this class, is the vitreous mass left on distilling crude turpentine with water (see **Exp. 116, § 251**). It burns with a

smoky flame, and is used in the preparation of lamp-black (§ **181**) and cheap varnish. Gum copal, mastic, sandarach and shellac are resins. The resins are insoluble in water, but dissolve in alcohol, wood naphtha (§ **230**), naphtha and oil of turpentine. The solutions thus obtained are called **varnishes.** When exposed in a thin layer to the air, the solvent evaporates, leaving a transparent coating of the resin, which protects the varnished surface from air and moisture.

Exp. 144. — Powder 3 grms. of shellac, mix with a quantity of clean sand and pour upon it 30 c. c. of alcohol. Allow to stand until the shellac has dissolved. Pour a portion of the solution into water : the shellac is precipitated, as it is insoluble in water.

317. The resins seem in many cases to be formed by the oxidation of the essential oil of the plant by which they are produced, and it is a familiar fact that when oil of turpentine is exposed to the air it absorbs oxygen, and is converted into a sticky, resinous substance. During the oxidation ozone is produced, and its effects are manifested by its bleaching action on the corks of the bottles in which the oil of turpentine is kept.

The resins are made up in the main of several acid bodies, of which *resinic acid* is the principal. By the action of bases on resin, bodies called *resinates* are formed ; thus sodium resinate, formed by the action of caustic soda on common *rosin*, is used in the manufacture of some kinds of soap ; it is soluble in water and valuable on account of its detergent properties. *Lead resinate* is insoluble in water and alcohol.

Exp. 145. — Dissolve a small amount of powdered rosin in alcohol : dissolve also a portion of crystallized lead acetate in 10 times its bulk of alcohol. Mix the two solutions and observe the formation of a bulky white precipitate of *lead resinate.*

318. **Gum Resins** are exudations from many plants which, being first milky, afterwards solidify in the air ; such are assafœtida, gamboge, myrrh, olibanum, etc. **Gutta-percha** is a tough, elastic substance insoluble in water, which issues as a milky juice from cuts in the trunk of a species of tree which grows in the East Indies. Gutta-percha is a mixture of a hydrocarbon ($C_{20}H_{32}$) and several resins. **Caoutchouc** or **India-rubber** is the solidified juice of certain tropical

plants. It is mainly a mixture of several hydrocarbons ($x\ C_5H_8$). It is insoluble in water, but when treated with ether, carbon bisulphide, oil of turpentine or benzol, it swells up in a very remarkable manner, and finally forms a sort of solution.

Exp. 146. — Into a small bottle put several teaspoonfuls of oil of turpentine, and add a few clippings of sheet caoutchouc. Cork the bottle and allow it to stand for some time. The caoutchouc swells up to many times its original bulk, and eventually dissolves.

319. **Caoutchouc** is very elastic, and freshly-cut edges readily reunite. When exposed to the light and air for some time, it absorbs oxygen and is converted into a sticky mass. Caoutchouc may be made to take up and combine with a certain proportion of sulphur, forming what is called **vulcanized India-rubber.** This mixture preserves its consistency and its elasticity through all ordinary changes of temperature, and is not affected by exposure to light. Heated to a certain temperature, the vulcanized caoutchouc is converted into a hard mass resembling horn, and called "hard rubber," vulcanite or ebonite. India-rubber and gutta-percha are largely used in the manufacture of water-proof clothing, tubing for conveying liquids and gases, combs, buttons, picture-frames and a great variety of other articles.

320. **Amber** is one of a number of fossil substances resembling the resins. Amber is found principally along the shores of the Baltic, but also occurs in beds of lignite in other localities. It becomes highly electric on friction. Chemically it is a mixture of several resinous bodies; it also contains a peculiar acid called *succinic acid.* Only about an eighth part is in its natural state soluble in alcohol; but after fusion it dissolves quite readily and is used in the preparation of varnish.

321. **Vegetable Acids.** — Among the important products of the vegetable kingdom are the **organic acids** which occur ready formed in plants, either in the free state or in combination, as salts of certain metallic elements or radicals. The occurrence of the salts of several of the fatty acids in the oils of plants has

already been noticed. The salts of oleic acid (§ **241**) and other acids classed with it also exist in vegetable fats and oils. The acids which are to be considered in this place generally occur as salts of calcium or potassium.

322. **Oxalic acid** ($C_2H_2O_4$) occurs as potassium oxalate and calcium oxalate in the juice of the sorrel, rhubarb and many other plants. Calcium oxalate, though insoluble in water, is somewhat soluble in the juices of the plant: it is, however, sometimes found in microscopic crystals in the cells of the plant. Oxalic acid is very poisonous when taken internally; the best antidote is chalk (calcium carbonate) or magnesia, as the oxalates of calcium and magnesium are quite insoluble compounds.

323. On a large scale oxalic acid is prepared by making a thick paste of sawdust with a strong solution of caustic potash and caustic soda and heating the mixture on iron plates. The woody fibre is converted into oxalic acid, and sodium and potassium oxalates are formed from which the acid is extracted. On a small scale oxalic acid is best prepared by the action of nitric acid on starch or sugar.

Exp. 147. — In a flask of 500 c. c. capacity, heat gently 100 c. c. of nitric acid of 1.38 sp. gr. and 10 grms. of starch. The experiment should be performed where there is a good draught of air, as nitrous fumes are copiously evolved. When the evolution of the fumes has nearly ceased, the solution is transferred to an evaporating dish and slowly evaporated to about one-sixth its bulk. On cooling the solution, oxalic acid will be obtained in transparent crystals.

324. **Oxalic acid** occurs in crystals having the formula $C_2H_2O_4 + 2\,H_2O$. The crystals lose the water of crystallization when dried at 100°, and at the ordinary temperature of the air they effloresce somewhat. The crystals are much more soluble in hot than in cold water. Oxalic acid dissolves the metallic oxides with facility, forming **oxalates**: on this fact depends its use in cleaning articles of brass and copper, and in removing spots of iron-rust and ink.

Exp. 148. — Dip a piece of white cloth in common writing-ink,

and when dry immerse it in a solution of oxalic acid, made by dissolving 2.5 grms. of oxalic acid in 50 c. c. of water. Then rinse the cloth in water : the color will be discharged.

Writing-ink owes its color to a tannate of iron (§ 331), which on exposure to the air becomes nearly insoluble in water. The oxalic acid destroys this compound and forms with the iron a soluble combination.

325. From the formula of oxalic acid, $C_2H_2O_4(H_2O,C_2O_3)$, the existence of an anhydride C_2O_3 might be inferred, an oxide of carbon intermediate between **CO** and CO_2. Such anhydride has, however, never been obtained. When oxalic acid is treated with strong sulphuric acid it is broken up, the sulphuric acid retaining the H_2O, and the C_2O_3 dividing into **CO** and CO_2. In fact, this is a common way of making carbon protoxide. By distilling alcohol with oxalic acid, oxalic ether or ethyl oxalate is obtained $(C_2H_5)_2C_2O_4$.

326. **Malic acid** ($C_4H_6O_5$) occurs abundantly in unripe apples, and in most acid fruits, such as the gooseberry and currant. As potassium malate, it occurs in the rhubarb, and crystals of this salt may be obtained by evaporating the juice of the leaf-stalks. Calcium malate occurs in sumach berries and in the sap of the maple. In boiling down the maple sap to obtain the sugar, fine, hard crystals of calcium malate often separate. Malic acid may be obtained in crystals, but they are extremely soluble in water, and deliquesce in moist air.

327. **Tartaric Acid** ($C_4H_6O_6$). — Tartaric acid occurs in a great variety of plants : the commercial supply is obtained from the grape. All varieties of wine during fermentation deposit on the insides of the casks a crust called **argol**. This argol or crude tartar is a hydrogen potassium tartrate, commonly called "**bitartrate of potash**;" when purified, it is called "**cream of tartar**:" from argol or cream of tartar tartaric acid itself may be obtained in transparent crystals, which are permanent in the air.

Exp. 149. — Dissolve 20 grms. of cream of tartar in 150 c. c. of hot water, to which 10 c. c. of strong chlorhydric acid have been added. To the solution add milk of lime (made by stirring 20 grms. of slaked lime, calcium hydrate, into 100 c. c. of water) until the solution shows a distinctly alkaline reaction. Insoluble calcium tar-

trate settles to the bottom of the liquid, and should be collected on a filter and washed. Transfer this calcium tartrate to a flask, add 100 c. c. dilute sulphuric acid (made by adding 10 grms. oil of vitriol to 100 c. c. water), and boil for some minutes. The sulphuric acid causés the formation of calcium sulphate, and free tartaric acid is left in the liquid. The insoluble calcium sulphate is removed by filtration ; the filtrate is concentrated by evaporation over the lamp to the bulk of 20 c. c. and allowed to cool. Crystals of tartaric acid separate from the liquid. These crystals are drained from the mother liquor and pressed between pieces of filter-paper ; they may be purified by dissolving them in half their weight of boiling water, and allowing the solution to cool, when a considerable part of the acid crystallizes out again.

328. **Tartaric acid** finds important applications in the art of dyeing, and many of the **tartrates** are important compounds : Rochelle salt is a sodium potassium tartrate : tartar emetic is an antimony potassium tartrate ; both these salts are used in medicine. The so-called " Rochelle powders " contain cream of tartar in one paper, and hydrogen sodium carbonate in the other ; when the two materials are mixed in water, carbonic acid is set free, and Rochelle salt remains in solution.

Exp. 150. — Dissolve 10 grms. cream of tartar in 175 c. c. of hot water, and to the solution add a strong solution of sodium carbonate as long as the addition produces effervescence. Evaporate the solution over the lamp to the bulk of 20 c. c. and then allow it to cool. Crystals of Rochelle salt will be obtained.

329. **Citric acid** ($C_6H_8O_7$) occurs very abundantly in the juice of the lime and the lemon, and has been found in the tomato and in most acid fruits. It may be obtained crystallized, with one equivalent of water, in large transparent crystals. It has a sour, but rather agreeable taste. It is used by the calico-printers, and to some extent in medicine, especially as magnesium citrate.

330. **Tannic Acid.** — **Tannin** is the general name applied to an astringent principle contained in the leaves and bark of many forest trees, such as the oak, hemlock and pine. Similar substances occur in the leaves and bark of many fruit-

trees, in the roots of certain plants, as well as in coffee and tea. These substances possess an acid reaction, and several distinct acids have been identified in them ; the **tannin** derived from gall-nut is called **gallo-tannic acid**; that from oak bark is called **querci-tannic acid**; that from coffee, **caffeo-tannic acid.**

331. The principal applications of **tannic acid** in the arts are in the preparation of writing-ink, and in the manufacture of leather.

Exp. 151. — Boil 10 grms. of powdered nut-galls in about 60 c. c. of water for several hours, replacing from time to time the water lost by evaporation : a solution of tannic acid is thus obtained. Allow the mixture to settle, and decant the clear liquid into a clean bottle. To a portion of this solution add a few drops of a solution of copperas (iron sulphate). A violet-colored precipitate is formed, which gradually changes to black ; it is an *iron tannate.* If the solution of tannic acid were made viscous by the addition of a little gum, the precipitate would remain suspended in the liquid. Common ink is made from these materials.

Exp. 152. — To another portion of the tannic acid solution, add a few drops of a solution of gelatin or isinglass. A copious white gelatinous precipitate falls.

On the property just illustrated, of uniting with gelatinous matters to form insoluble compounds, depends the use of tannic acid in tanning. If a piece of raw hide from which the hair has been removed be immersed in an infusion of the bark, the gelatinous matters of the hide gradually remove the tannic acid from the solution, and combine with it to form an insoluble compound, which remains in the structure of the hide : the skin thus altered is leather.

332. In **Exp. 151,** it was seen that a solution of a salt of iron was blackened by the addition of a solution of tannic acid derived from gall-nuts. This reaction may be made use of as a **test** to demonstrate the presence of **tannic acid.**

Exp. 153. — Boil a few tea-leaves in a small amount of water, and to the liquid add a drop or two of a solution of copperas. The liquid is blackened, and after a time a black precipitate of iron tan-

nate subsides. The presence of tannic acid may be shown similarly in coffee, in hemlock bark, in horse-chestnut husks, etc.

333. **Gallic Acid.** — The gall-nuts used in Exp. 151 are excrescences produced on a species of oak by the punctures of a certain insect. Besides tannic acid, the nut-galls contain a small percentage of another acid, **gallic acid.** **Gallic acid** may also be produced by boiling a solution of tannic acid (from nut-galls) with dilute sulphuric acid. The composition of gallo-tannic acid is $C_{27}H_{22}O_{17}$; when boiled with dilute sulphuric acid, it unites with the elements of water, and forms **gallic acid** and **glucose** (§ 294).

$$\underset{\text{Tannic acid.}}{C_{27}H_{22}O_{17}} + 4\,H_2O = 3\,\underset{\text{Gallic acid.}}{C_7H_6O_5} + \underset{\text{Glucose.}}{C_6H_{12}O_6}.$$

Tannic acid is the representative of a class of bodies, which, by a reaction analogous to that represented above, yield glucose : they are hence called **glucosides.**

334. **The Vegetable Alkaloids** or organic bases occur in small quantities in various plants of which they constitute the medicinal or poisonous principles. They occur in combination with some acid which is generally peculiar to the particular plant in which they are found. They are only slightly soluble in water, but are readily dissolved by alcohol. They resemble ammonia in containing nitrogen, in having an alkaline reaction, and in uniting directly with acids to form salts, which as a rule crystallize readily.

335. **Opium** is the dried juice of the poppy. It contains besides certain gummy, resinous and oily bodies no less than six alkaloids in combination with a peculiar acid called *meconic acid.* Of these alkaloids **morphia,** or **morphine,** is the most important as a medicinal agent. It is usually administered as sulphate or chloride. Morphine or opium in small doses acts as a sedative, in large doses as a narcotic poison.

Strychnine is a highly-poisonous alkaloid which occurs in the St. Ignatius bean and in the nux vomica, associated with **brucine.** Of the two, strychnine is the more violent poison, although both are very powerful in their effects on the living organism.

The bark of the **cinchona,** a tree found native in Peru, contains several bases, of which the most important are **quinine**

and **cinchonine.** Quinine possesses valuable medicinal properties, and is used as a febrifuge; cinchonine is also employed as a medicine, but is of less value than quinine.

Caffeine or **Theine** occurs in tea and coffee, and may be obtained therefrom in white crystals; **theobromine** occurs in cacao; **nicotine** is the chief alkaloid in tobacco, and is a very violent poison.

336. **Organic Coloring Matters.** — Nearly all of the organic coloring matters used in dyeing are of vegetable origin. They occur sometimes in the roots, sometimes in the stems or bark, sometimes in the flowers or even in the seeds of the plant from which they are derived. Some coloring matters occur ready formed in the plant, others are the result of the action of the air or some other chemical agent upon natural products. These substances in many cases are not chemically related to each other, but they are classed together on account of their association in the arts. A few of the more important will be here mentioned.

337. **Madder** is the root of a plant which was formerly grown in the East, in the south of France and in some other localities in Europe, and used principally in dyeing reds and purples. The coloring matters do not exist ready formed in the plant, but are produced by the decomposition of a body contained in it. The principal coloring matter, and the one to which madder owes its value, is a substance called **alizarin** ($C_{14}H_8O_4$). Reducing agents convert alizarin into a hydrocarbon identical with the anthracene ($C_{14}H_{10}$) which occurs in coal-tar (§281); and since chemists have succeeded in preparing alizarin artificially from anthracene, the artificial dye-stuff has displaced almost entirely the natural product.

Among other organic coloring matters used in dyeing various red dyes are Brazil-wood, logwood, safflower and cochineal. The last is a dried insect, which, when alive, lives on a tropical plant, a species of cactus. The coloring matter, *carmine*, is soluble in water.

Exp. 154. — Boil 2 grms. of crushed granules of cochineal in 75 c. c. water for some minutes. Filter the colored solution and preserve for use in subsequent experiments.

338. Yellow dye-stuffs are *quercitron*, obtained from the bark of a variety of oak, *fustic*, from the wood of a West-Indian tree, *turmeric* from the root of an East-Indian plant, and a coloring matter obtained from "Persian berries." Certain species of lichens also yield coloring matters; the dye-stuffs known as *archil*, *cudbear* and *litmus* are derived from such sources.

339. **Dyeing.** — One method of dyeing fibres or fabrics of animal and vegetable origin has been illustrated by **Exp. 130,** in which simple immersion of the wool in the solution of picric acid sufficed to give it a yellow color.

Exp. 155. — Into a warm solution of picric acid prepared as directed in Exp. 130 put a piece of cotton cloth or a skein of cotton yarn. After the cotton has been immersed in the solution for some time, take it out and rinse it with water. It will be found that the cotton is not colored.

This experiment illustrates a very important difference between the fibres of vegetable and those of animal origin. Of almost all the vegetable coloring matters, it is true, that they do not directly produce fast colors on cotton or linen, while they readily color articles of wool.

Exp. 156. — Prepare a solution of the coloring matter of logwood by dissolving 1 grm. of extract of logwood in 75 c. c. water. Allow the liquid to stand for a short time until it becomes nearly clear, and then decant it from any insoluble matter which may subside. Place a quantity of the nearly clear solution in a porcelain evaporating-dish, put into it a piece of cotton cloth 5 or 6 c. m. square and boil for some 10 minutes. On removing the cloth, it will be found possible to wash out most of the dye, leaving the cloth only slightly colored.

Exp. 157. — Into a quantity of logwood solution equal to that employed in the last experiment, put a piece of cotton cloth 5 or 6 c. m. square which has previously been soaked, first in a solution of common alum, and then in ammonia-water. Boil the solution, as in the previous experiment. When the cloth is removed, it will be found to be quite strongly colored.

This experiment illustrates the fact that it is possible to impregnate the cloth with certain substances which have the power of dragging

in the coloring matter and holding it firmly. Such substances are called **mordants**, and as they are generally compounds of some of the metals, their action will be better studied hereafter (§ 451).

340. **Indigo.** — Of the vegetable dyes, one of the most important, and one which possesses considerable chemical interest, is **indigo** used, as is well known, in producing a very permanent blue color. Crude indigo contains a blue coloring matter which, when purified, is known as **indigotin** or **indigo-blue.** Its formula is $C_{16}H_{10}N_2O_2$, and it differs from the other coloring matters previously mentioned in that it contains nitrogen. The blue coloring-matter does not occur ready formed in the plant, but is produced by a sort of fermentation. Indigo-blue is insoluble in water or in alkaline liquids, but dissolves in fuming sulphuric acid (§ **135**), forming a deep blue solution.

Exp. 158.—Upon 1 grm. of finely powdered indigo pour 6 grms. of fuming sulphuric acid and let the mixture stand for some hours in a warm place. On the addition of water a deep blue solution is obtained. Ordinary strong sulphuric acid will dissolve indigo, but it is necessary to take a much larger quantity (in this case about 12 or 14 grms.), and to heat the mixture to about 60° ; moreover, when thus heated a portion of the blue coloring-matter is destroyed.

341. The deep blue liquid formed by the action of sulphuric acid on indigo contains at least two acid compounds. The solution is, however, commonly spoken of as **sulphindigotic acid,** and is used just as made, or partially neutralized with sodium or potassium carbonate, in dyeing the color known as Saxon blue, and in the preparation of various sorts of bluing.

342. When **blue indigo** is treated with reducing agents, it is converted into a colorless compound soluble in alkaline liquids and known as "**white indigo.**" On exposure to the air, the white indigo is reconverted into insoluble indigo-blue.

Exp. 159. — Into a test-tube put as much finely powdered indigo as can be taken on the point of a small penknife, and half a teaspoonful of fine zinc filings (*zinc dust* is best if it can be obtained). Pour into the test-tube two teaspoonfuls of a moderately strong solution of caustic soda and heat the mixture : the caustic soda acts upon the zinc and hydrogen is set free : by the action of the nascent hydro-

gen the indigo-blue is converted into white indigo, and the white indigo dissolves in the alkaline liquid, forming a yellowish solution.

The formula of white indigo is $C_{16}H_{12}N_2O_2$. When an alkaline solution of white indigo is exposed to the air, it is converted into indigo-blue :—$C_{16}H_{12}N_2O_2 + O = C_{16}H_{10}N_2O_2 + H_2O$.

Exp. 160. — Pour out a portion of the solution of the preceding experiment into a shallow dish and observe that in contact with the oxygen of the air insoluble indigo-blue is formed.

Exp. 161. — Dip a piece of white cloth or filter paper into the liquid remaining in the test-tube. As soon as the moistened cloth or paper comes out into the air it will turn blue.

The experiment illustrates the method actually employed to some extent in dyeing with indigo. Other reducing agents are also used (very commonly a mixture of slaked lime and copperas), the action of which will be better understood hereafter. The cloth dipped into the solution of white indigo becomes thoroughly impregnated with this solution, and when the indigo-blue is formed, it is formed within and among the fibres of the cloth, so that the color is "fast."

343. **Physiological Chemistry.** — The study of the various fluids and solids occurring in the living animal, and concerned in the processes of circulation, respiration and digestion, belongs more particularly to that branch of the science designated as **physiological chemistry,** and is not fitted for an elementary manual.

The chemical relations of the substances concerned in the vital functions are, as a rule, but imperfectly understood, and many of the substances themselves are extremely complex ; thus to **albumin** has been assigned the formula $C_{72}H_{112}N_{18}SO_{22}$, but such formulæ are to be regarded only as rough approximations. Bodies of like complexity also occur in vegetables, although the mass of the plant is made up, as we have seen, of substances comparatively simple in composition. The more particular study of the chemical phenomena involved in the growth, nutrition and decay of plants belongs to **agricultural chemistry.**

In this place, brief mention will be made of a few of the more important compounds which occur in animals and plants, and which have not as yet been considered.

344. **Albumin** occurs abundantly in many of the fluids and soft solids of the animal body. It is most familiar as the *white* of the eggs of birds ; it is found also in considerable proportion in the blood, although blood-albumin differs in some of its characters from egg-albumin. The most striking properties of albumin are its solubility in water, and its coagulation by heat and other agents ; these properties may be exhibited with fresh white of egg.

Exp. 162. — Beat or whip the white of an egg to destroy the transparent membrane of the cells in which the albumin is held, and agitate a portion with water : it dissolves readily.

Exp. 163. — Add strong alcohol to a portion of the solution obtained in Exp. 162. The albumin is coagulated.

Exp. 164. — Place a little of the albumin in a test-tube, put the tube into water, contained in a beaker or evaporating-dish, and heat the dish. Observe that the albumin coagulates some time before the water is hot enough to boil ; namely, at about 60°.

Albumin is a very complex compound of carbon, hydrogen and oxygen, and contains also a certain proportion of nitrogen and sulphur. A body of similar composition occurs in vegetables, and is called *vegetable albumin*. To the presence of sulphur in albumin, and in a somewhat similar body which occurs in the yolk of eggs, is due the peculiar odor of rotten eggs ; to the same presence is owing the fact, that silver spoons used in eating eggs are stained, silver sulphide being formed.

345. **Fibrin** occurs in the animal body in a soluble and in an insoluble state. In the soluble state it occurs in the blood ; but when exposed to the air this fibrin coagulates and forms the *clot*. By washing the clot with water, a white, stringy mass of fibrin is obtained. In the insoluble state it forms the fibres of muscle ; it may be obtained by washing a piece of lean meat repeatedly until the coloring matter is removed. In composition fibrin approaches albumin, but contains more oxygen and nitrogen than albumin. A similar body called **vegetable fibrin** occurs in *gluten*.

346. **Casein** occurs in the milk of animals. It bears some resemblance to albumin, but is not coagulated by heat. It is coagulated by acids and by **rennet,** the inner membrane of

the stomach of the calf. Advantage is taken of this fact in the manufacture of cheese, which is made by warming the milk in contact with rennet; the casein is coagulated and rises to the surface carrying with it the fatty matters held suspended in the milk. The **curd** thus obtained when pressed is **cheese.**

347. **Milk** consists mainly of water holding in solution casein, milk-sugar and certain salts, such as sodium and potassium chlorides, and the phosphates of calcium, magnesium and the alkaline metals. It holds in suspension a number of oily globules, and when allowed to stand quietly these globules rise to the surface, forming the *cream.* The residue, after the removal of the cream and the coagulation of the casein, is the *whey.* **Butter** is made by agitating the cream, so as to break up the little globules of oily matter, and allow it to collect together in one mass.

Exp. 165. — Allow some fresh milk to stand until the cream has risen to the surface. Remove the cream by skimming, and to the skimmed milk add a little dilute sulphuric acid. The milk is *curdled*, that is, the casein is coagulated and rises to the surface.

348. **Legumin** is a substance which resembles casein; it occurs in peas, beans, etc. The Chinese make a sort of vegetable cheese from peas.

349. **Gelatin and Glue.** — **Gelatin** is a body consisting of the same elements as albumin, but in somewhat different proportions. Gelatin is obtained when the bones or skins of animals are boiled in water. It is soluble in boiling water, but the solution gelatinizes on cooling. **Glue** is an inferior variety of gelatin, made from the parings and refuse of ox-hides. **Isinglass** is made from the swimming-bladder of sturgeons and other fishes, and is nearly pure gelatin.

Gelatin does not occur ready formed in the bones, skin, etc. but is produced by the action of boiling water on a substance so contained. This substance is called **ossein;** a somewhat similar substance, which occurs in the shells of lobsters and crabs, and in the skins of earthworms, is called **chitin.**

Exp. 166. — Immerse a *clean* bone in dilute chlorhydric acid (made by diluting the commercial acid with six times its bulk of water). The mineral part of the bone will gradually dissolve away, and after three or four days there will be left a flexible substance which preserves the shape of the bone, and when dry has a translucent, horny appearance. This is *ossein.*

Exp. 167. — Boil the ossein of Exp. 166 with water for several hours. It dissolves almost entirely, being converted into gelatin. Allow the solution to cool ; it will gelatinize.

350. **Decay of Organic Substances.** — Organic substances, partly on account of the complexity of their structure, are very liable to undergo change. This is especially true of substances, which are the immediate product of animal or vegetable life. The ultimate or final products of the decay of animal or vegetable matter are mainly carbonic acid and water, since the greater part of all organic matter is made up of carbon and hydrogen (and oxygen). This complete conversion takes place when the substances are exposed to a high temperature with free access of oxygen. In the ordinary processes of decay, however, a vast variety of intermediate products are formed, some of which are very offensive, especially when sulphur is an ingredient of the decaying substance. By the decay of substances containing nitrogen *ammonia* is formed, and, under certain conditions, *nitric acid: nitrates* are always found in the soil and in well waters of thickly inhabited localities, and *calcium nitrate* is made artificially by allowing nitrogenous organic matter, mixed with lime or plaster, to decay slowly in the air.

351. The intermediate products of the decay of organic substances are as a rule imperfectly known : certain forms of decay, such as the various sorts of **fermentation,** have been carefully studied, but in other cases, as in the slow decay of woody fibre in the soil, little is known with certainty on account of the difficulty of isolating the various compounds in a state of assured purity. Even in the case, however, of simple fermentation of grape-sugar, the chemical changes are by no means as simple as might at first appear from **Exp. 100, § 226.**

Although the reaction of § **193,** which represents the conversion of the sugar into carbonic acid and alcohol, expresses the main reaction which occurs, yet, in addition to these products, there are formed several other bodies in greater or less amount: thus *lactic* and *succinic acids, glycerin* and a brown substance resembling *caramel* are among the usual products of alcoholic fermentation.

352. The natural decay to which dead organized bodies are prone may be arrested more or less completely by the use of certain chemical agents, or in some cases by the simple exclusion of air. Warmth and moisture are among the conditions favorable for the beginning of decomposition; in a cold climate or in winter, animal substances may be kept for a much longer period than in summer.

Among the chemical substances used as **antiseptic** or **preservative agents** are common salt, which is used in the curing of meat and fish; wood-smoke, which owes its virtue to the kreasote (§ **282**) contained in it, and which is used in the smoking of hams and other articles of food; kreasote itself and carbolic acid, the use of which was illustrated in **Exp. 128;** and the dead oil of tar (§ **275**), used in preserving timber. The effect of the exclusion of air is illustrated in the canning of fruits; also by the domestic processes of "preserving" fruits by immersion in strong sirup.

CHAPTER XVIII.

SILICON AND BORON.

SILICON (si).

353. After oxygen, **silicon** is the most abundant and widely diffused of all the chemical elements. It occurs in combination

with oxygen as **silica** and in combination with oxygen and various metallic elements as **silicates** of those elements.

354. **Silicic anhydride** or **Silica** (SiO_2) occurs in nature as quartz, flint, rock-crystal, agate, etc. It occurs also in plants, particularly in the outer covering of the stalks and the husks of grain. The cuticle of rattan, for example, contains a large proportion of silica, and the same remark is true of most of the grasses and grains. The value of the plant called horse-tail (*Equisetum*) as a polishing or scouring agent depends upon the large quantity of silica contained in it.

355. As it occurs in nature, **silica** is insoluble in water, but dissolves with more or less difficulty in caustic soda (or potash), forming sodium (or potassium) silicate. The potassium and sodium silicates are used in the arts under the name of **water-glass** or **soluble glass.**

Exp. 168. — To a concentrated solution of water-glass contained in a small evaporating-dish, add enough strong chlorhydric acid to make the solution acid. There will separate a thick jelly-like mass of silicic acid (H_4SiO_4). Evaporate the contents of the dish to dryness on a water-bath, and then heat the residue gently over the gas-lamp. The mass will contract in bulk, and, on adding water, there will remain undissolved a fine white powder of silicic anhydride.

Exp. 169. — Take a very dilute solution of water-glass, and add dilute chlorhydric acid drop by drop until the liquid has a decidedly acid reaction. No precipitation will occur : the silicic acid which is set free, as in the preceding experiment, remains dissolved in the acid liquid.

It is possible, also, to prepare an aqueous solution of silicic acid, but if these solutions be evaporated to dryness and the residues heated, there is formed in each case the insoluble silicic anhydride.

356. **Silicates.** — Silicic anhydride combines with many of the metallic oxides to form **silicates.** Hundreds of silicates occur in nature as crystallized minerals ; thus ordinary feldspar is a double silicate of aluminum and potassium, common mica is a complex silicate of aluminum, iron and potassium.

357. **Glass.** — Besides the silicates which occur in nature, there are artificial silicates of great importance in the arts and in every-day life. Sodium silicate (water-glass), which has already been alluded to, is extensively used by calico-printers and soap-makers. Its chief use, however, is as a component of common **glass.** The various glasses of commerce are mixtures of a highly silicious silicate of sodium, or of potassium, or of both these substances, with silicates of other metals, such as calcium, aluminum and lead. The silicates of the alkaline metals are non-crystalline and soluble in water, the silicates of most of the other metals have a tendency to assume the crystalline form. It has been found that, by combining the alkaline silicates with the silicates of certain other metals, such as calcium, there may be obtained compound glasses which, while they retain the amorphous character of the alkaline silicates, are capable of resisting the action not only of air and water, but even of acids and alkalies, to a very great extent; thus, ordinary window-glass is composed of silicates of sodium and calcium; Bohemian glass, suitable for ignition-tubes, consists of silicates of potassium and calcium; flint-glass contains silicates of potassium and lead. Bottle-glass is a mixture of silicates of calcium, aluminum, iron and sodium. The silicates of some of the metals are colored: the green color of bottle-glass is due to the presence of ferrous silicate; cobalt silicate gives a beautiful blue, manganese silicate a violet and uranium silicate a yellow color to the glass.

358. **Silica** and the **silicates** are readily attacked by **fluorhydric acid,** as has been already seen (**Exp. 41, § 100**). When silica is treated with dry fluorhydric acid gas, there is formed a gaseous compound known as **silicon fluoride** (SiF_4) which, in contact with water, decomposes into gelatinous silicic acid, and another compound known as **fluo-silicic acid** ($2\,HF,SiF_4$): —

$$3\,SiF_4 + 4\,H_2O = SiH_4O_4 + 2\,(2\,HF,SiF_4)$$

Exp. 170. — Into a perfectly dry tube of hard glass, No. 5, closed at one end, drop a small quantity (as much as can be taken on the

point of a penknife) of a mixture of equal parts of fine quartz sand and powdered fluor-spar (calcium fluoride). Moisten the mass with a drop of strong sulphuric acid, and heat in the flame of the lamp. Gaseous silicon fluoride will escape from the tube, and if a drop of water in the loop of a bit of platinum wire, or on a colored glass rod, be held at the mouth of the tube, the water will become cloudy from the deposition of silicic acid.

Fig. 63.

359. **Silicon** (**Si**) may be obtained pure from a compound known as potassium fluo-silicate. Three **allotropic conditions** are known corresponding to the three modifications of carbon (§ **174**). The amorphous variety is a brown powder which burns readily in air or oxygen, forming silicic anhydride (SiO_2). The atomic weight of silicon is 28.

360. **Silicon in Organic Compounds.** — The most important of the organic compounds containing silicon are the so-called silicic ethers or the silicates of the organic radicals; thus methyl silicic ether is $(CH_3)_4SiO_4$; ethyl silicic ether is $(C_2H_5)_4SiO_4$, etc. These are all artificial bodies; they are volatile, colorless, inflammable liquids having generally an ethereal odor.

BORON (B).

361. **Boron** is found in nature in combination with oxygen, as **boracic acid,** and in combination with oxygen and some metallic element, the most important compound being **sodium biborate,** commonly called **borax.**

In certain volcanic districts in Tuscany, jets of steam mixed with other vapors escape continually from cracks in the soil, and bring to the surface small quantities of boracic acid. Since boracic acid is not volatile, in the ordinary sense of the term, at temperatures as low as 100°, it appears that it is transported mechanically by the steam, much in the same way that dust is carried along by a current of air. The jets of vapor, laden with boracic acid, are made to bubble through water as they escape from the earth, and the solution thus

obtained is evaporated in pans, beneath which hot currents of vapor from the earth are caused to circulate, until it is concentrated to such a point that on cooling the boracic acid crystallizes out.

362. **Boron** (B). — Of boron itself little need be said. It resembles carbon in that it may be obtained in an amorphous condition like charcoal, and also crystallized like the diamond. The atomic weight of boron is 11.

363. **Boracic acid** (H_3BO_3) is but a feeble acid at ordinary temperatures; it may be set free by treating any borate with almost any acid, excepting carbonic acid.

Exp. 171. — Dissolve 4 grms. of powdered borax in 10 grms. of boiling water, in a beaker-glass or porcelain capsule of 30 or 40 c. c. capacity, and add to the solution 2.5 grms. of concentrated chlorhydric acid. As the solution cools, boracic acid will be deposited in the form of glistening, colorless plates or scales.

364. **Boracic acid** imparts to the flame of burning alcohol a peculiar green tint, which is quite characteristic, and affords a valuable test by which the presence of the acid may be detected.

Exp. 172. — Dissolve a little crystallized boracic acid in a teaspoonful of alcohol in a small porcelain capsule. Set fire to the alcohol and stir the burning solution with a rod, or agitate it by jarring the dish. The flame of the alcohol will be of a fine green color.

365. **Boracic anhydride** (B_2O_3) may be prepared by heating crystallized boracic acid, as follows.

Exp. 173.—In a clean iron spoon heat some crystallized boracic acid. The crystals will melt, and if the heat be continued, the mass will become pasty, and will swell up as the water is expelled. After all the water has been driven off by strong heat, the anhydride is left as a clear, viscous liquid, from which long threads may be drawn out by touching to the surface of the liquid the end of a stick or glass rod, and then gently pulling away the stick with the matter which has adhered to it.

If the fused mass be allowed to cool, it will solidify to a hard, transparent glass, which soon cracks in every direction and splits up into fragments.

CHAPTER XIX.

SODIUM (Na).

366. This abundant element is chiefly found in nature in the state of chloride, nitrate, carbonate, borate and silicate. The most abundant of its compounds is common **salt,** which is the combination of sodium with chlorine (**NaCl**). On account of the inexhaustible abundance of common salt, this substance constitutes the chief source from which all manufactured compounds of sodium are more or less directly derived; one other natural sodium-containing mineral, however, deserves mention as a source of sodium compounds, — the mineral **cryolite,** — a double fluoride of sodium and aluminum (§ **98**).

367. **Sodium Chloride** or **Common Salt** (**NaCl**). — This natural mineral is, when pure, a colorless, transparent, anhydrous stone, which crystallizes in cubes, dissolves readily in about three times its weight of cold water, and possesses a specific gravity of 2.15, and an agreeable taste, which, because familiar, is the representative or type of that peculiar savor called **saline.** A saline taste means a taste suggestive of that of common salt, just as the phrase, "**saline substance,**" characterizes a very large class of bodies which resemble more or less in appearance and properties the longest and best known of all such substances, — common salt.

There are three sources of salt, — the beds of the native mineral, saline springs and sea-water. In all cases in which the salt is obtained from its solution in water, evaporation by fire, or by the heat of the sun in warm, sunny climates, is necessary. When pure enough, the rock-salt is mined like any other ore, but when it is mixed with earth or other impurities, as it lies in its natural bed, the solubility of the sodium chloride in water is availed of to free the salt from its insoluble impurities, and to facilitate the lifting of it to the surface of the earth. Water is let in to the bed of salt, and allowed to remain there till it has become saturated; the brine is

then pumped out and evaporated. Some natural brine-springs contain so small a proportion of salt that some cheaper mode of evaporation than by fire is essential to their profitable working. Such waters are concentrated by a process termed *graduation*. The brine is pumped up to a sufficient height, and then allowed to trickle slowly over large stacks of fagots, which are sheltered by a roof from rain, but are freely exposed to the prevailing wind. The brine, thus diffused over a very large surface, is rapidly concentrated by the draught of air. By repeating the process a moderate number of times, a weak brine may be brought to a degree of concentration at which evaporation by fire may be employed. If the strong brine is boiled down rapidly, a fine-grained table-salt is obtained; if it is slowly evaporated, a hard, coarsely crystallized salt is the product. The thick *mother-liquor* from which no more sodium chloride will crystallize, contains the more soluble salts of the original brine, such as calcium chloride, magnesium chloride and bromide, besides a large proportion of common salt which cannot be separated from the liquor. Such mother-liquors are sometimes so rich in magnesium salts as to be advantageously worked for these substances, and they are also sometimes profitable sources of bromine. Considerable quantities of magnesium salts and of bromine have also been extracted from concentrated sea-water, after all the available sodium chloride has been withdrawn. The salt of commerce generally contains a small proportion of magnesium chloride, which makes it slightly deliquescent and bitter.

Exp. 174. — Dissolve 9 grms. of fine salt in 25 c. c. of water at the ordinary temperature. Add to the solution another gramme of salt; it will not dissolve. Bring the solution to boiling; the added gramme of salt will barely dissolve. Sodium chloride is scarcely more soluble in hot than in cold water, wherein it differs from the great majority of soluble salts. Evaporated brines deposit their salt with almost equal facility when hot and when cold, but the hot liquors will hold in solution a much greater proportion of the salts with which the sodium chloride is associated, than the cold brines could retain. In the process of evaporation by fire, the associated magnesium, calcium and sodium salts do not, therefore, crystallize with the common salt, but remain in the hot mother-liquor.

368. The uses of common salt are manifold; since it is a constituent of almost all kinds of food, and essential to the life of animals, it is not surprising that salt exists in small quantities in almost every spring, soil, plant and animal. The **antiseptic**

quality of salt is applied to the preservation of fish, meat and wood. Salt is extensively employed in glazing earthen-ware, its **volatility** at furnace-heat combining with other qualities to fit it for this use. Immense quantities of salt are consumed in preparing sodium sulphate, from which in turn common "**soda**" (sodium carbonate) is made. Salt is also the source from which chlorhydric acid is derived (§ **72**).

369. **Sodium sulphate** (Na_2SO_4) is made in great quantities from common salt and sulphuric acid as a preliminary step in the manufacture of sodium carbonate.

The process has two stages. The mixture of salt and sulphuric acid is first heated in large, covered cast-iron pans. As in Exp. 28, chlorhydric acid is disengaged from the mixture, and is absorbed by being passed through vertical stone towers filled with lumps of coke, over which water is kept trickling. The reaction which takes place in the iron pans is not complete, a portion of the sodium chloride remaining undecomposed. The reaction at this first stage may be represented as follows : —

$$2\,NaCl + H_2SO_4 = NaCl + HNaSO_4 + HCl.$$

The pasty mass is then pushed into an adjoining fire-brick chamber, which is strongly heated by flues from a furnace. The hydrogen sodium sulphate, of the last reaction, decomposes the remainder of the salt, and a further quantity of chlorhydric acid is disengaged to be condensed by the water in the coke-towers, while sodium sulphate remains : —

$$NaCl + HNaSO_4 = Na_2SO_4 + HCl.$$

The **sodium sulphate**, resulting from this process, is a white, anhydrous salt, which dissolves easily in water at 30°. When a strong solution of the anhydrous salt, made at this temperature, is cooled, there separate large, colorless crystals of a transparent salt, bitter and cooling to the taste. This salt, long known as **Glauber's salt**, contains, besides the elements of sodium sulphate, ten molecules of water ; it therefore answers to the formula, $Na_2SO_4.10\,H_2O$. The crystallized salt loses water on exposure to dry air ; it **effloresces** and is converted into the anhydrous salt.

Exp. 175. — Dissolve 10 grms. of crystallized Glauber's salt in water, the temperature of which has been previously observed ; during solution, the temperature falls, — cold is produced in consequence of the expenditure of some of the heat of the mixture in overcoming the cohesion of the crystallized salt. Dissolve a like quantity of effloresced Glauber's salt (anhydrous sodium sulphate) in a small bulk of water ; heat will be developed. A part of the water is solidified by combining with the anhydrous sulphate to form the hydrated sulphate, and the heat, which before kept that quantity of water fluid, being set free to do other work, raises by a certain amount the temperature of the mixture.

370. **Sodium Carbonate** (Na_2CO_3). — The manufacture of this substance constitutes one of the most important branches of chemical industry. Immense quantities of it are consumed in the fabrication of glass and soap, in the preparation of the various compounds of sodium, and in washing, both by the manufacturer of cloth and in the household. The ashes of sea and sea-shore plants were formerly the source of the sodium carbonate, but it is now chiefly made from common salt by a process called, from the name of its French inventor, **Leblanc's process.**

The first stage of this process we have already studied ; it consists in the preparation of the sodium sulphate from common salt. In the second stage, the sodium sulphate is mixed with coal and chalk, or limestone (calcium carbonate), and heated in a reverberatory furnace. The carbon of the coal takes oxygen from the sodium sulphate (Na_2SO_4), and would leave sodium sulphide (Na_2S) ; but, at the same time, an interchange takes place between the sodium sulphide and the calcium carbonate, forming sodium carbonate and calcium sulphide. The mass remaining after the reaction is complete is called "black ball" or "black ash." When cold it is systematically washed with warm water until all the soluble portions are extracted. The solution is evaporated in large iron pans by the waste heat of the reverberatory furnaces, and again calcined. The product of this heating is the *soda-ash* of commerce ; it is almost white, and generally contains about 80 per cent of pure anhydrous sodium carbonate. As some caustic soda is always contained in the black-ash, the solution is frequently concentrated until the carbonate crystallizes out, and the mother-liquor is used for the manufacture of caustic soda.

Fig. 64 represents a reverberatory furnace such as is used in the manufacture of wrought iron : the furnaces used in the manufacture of soda-ash differ in their details from the one figured, but the general principle is the same. In a reverberatory furnace the substance to be heated does not come into immediate contact with the fuel; the fire is built upon the grate-bars (G) and the flame plays over the hearth (H), the heat being reflected downward from the curved roof.

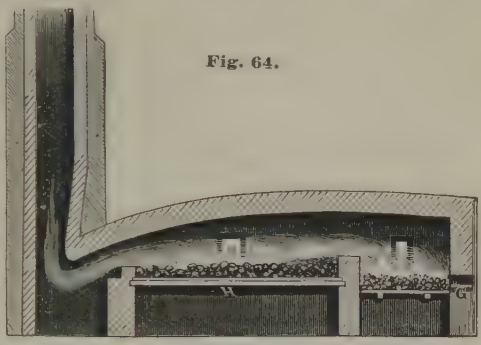


Fig. 64.

The so-called *crystals of soda* are obtained by dissolving the crude soda-ash in hot water, and suffering the hot solution to cool in large pans. In the course of five or six days, large transparent crystals are formed which contain 62.93 per cent of water, and correspond to the formula $Na_2CO_3,10\,H_2O$. The crystals effloresce in the air; they have a disagreeable taste, called alkaline, are soluble in very large proportion both in hot and cold water, and even melt at a moderate temperature in their own water of crystallization. The crystals readily part with all their water, and the dry residue melts at a bright red heat; this residue is anhydrous sodium carbonate, purified by the process of crystallization which it has undergone. In this case, as in all others, the process of crystallization consists essentially in the aggregation of *like* particles; the strong tendency is to exclude heterogeneous particles, or, in other words, impurities, from the crystallizing structure. There is no more universally applicable and valuable means of purification than the process of crystallization.

371. **Hydrogen Sodium Carbonate** ($HNaCO_3$). — When masses of crystals of hydrated sodium carbonate (soda crystals) are exposed to an atmosphere of carbonic acid gas, they absorb carbonic acid with an evolution of heat sufficient to expel the greater part of their water of crystallization. A white powder remains whose formula is $HNaCO_3$; the dualistic formula

(§ 153) is $Na_2O,H_2O,2\,CO_2$, whence its most familiar name, — **bicarbonate of soda.** This substance is one of the ingredients in most of the artificial yeasts used for **raising** bread, cake and puddings, and is known to grocers and cooks as "**soda,**" although the constituent which is really utilized is the carbonic acid.

From sodium bicarbonate, carbonic acid may be set free by almost any acid or acid salt. Effervescing powders consist of sodium bicarbonate in one paper and tartaric acid in another; when these two materials are mixed in water, carbonic acid is set free, and a double tartrate of sodium and potassium, called **Rochelle salt,** and used as a purgative, remains in the liquid (see § 328). When bread or cake is "raised" with "soda" and cream of tartar, the escaping carbonic acid is the agent in puffing up the dough, and the same Rochelle salt remains in the bread. Tartaric acid and cream of tartar having been dear in late years, a cheaper chemical yeast powder has been made from acid calcium phosphate; when this substance reacts within the dough with sodium bicarbonate, there remains in the bread a mixture of the phosphates of sodium and calcium. Alum is sometimes used for the same purpose. It is necessary to employ for such purposes, in connection with the bicarbonate, acids or acid salts which are solid, and not so corrosive as to be obviously dangerous and harmful.

372. **Sodium** (**Na**). — The element **sodium** is never found uncombined in nature, for the reason that in its elementary condition it cannot exist in contact with either air or water. It is, however, artificially prepared from sodium carbonate without serious difficulty, and it might be produced in considerable quantities if there were any large use for the element. The atomic weight of sodium is 23.

The properties of the element **sodium** are very curious. The substance, when freshly cut, or when melted under naphtha or in an atmosphere artificially deprived of oxygen, has the brilliant, white, metallic lustre of silver. Though possessing so eminently this characteristic property of the class of bodies called metals, and being like them a good conductor of heat and electricity, sodium is far from resembling the ordinary metals in other respects; thus it is lighter than water, having a specific

gravity of only 0.972, whereas the common metals are dense and heavy ; again, it is as soft as wax at common temperatures, and melts at a temperature below that of boiling water ; while it has none of the comparative permanence which characterizes lead, tin, copper, silver, gold and other familiar metals. If exposed to the air, even for a few seconds only, it tarnishes, and soon becomes covered with a coating of oxide. Hence the necessity of preserving the metal under some liquid which, like naphtha, contains no oxygen. We have already seen that it decomposes cold water (**Exp. 8**), setting free its hydrogen, and combining with its oxygen.

Exp. 176. — Cover the bottom of a large bottle (at least a litre-bottle) with hot water, drop in a piece of sodium as large as a small pea, and immediately cover the mouth of the bottle with a card or glass plate. The heat caused by the chemical combination of the sodium and the oxygen of the water is sufficient to inflame the hydrogen set free; the escaping hydrogen carries with it a small portion of the volatilized sodium, and therefore burns with an intensely yellow flame which is very characteristic of sodium compounds. The metal swims rapidly about on the surface of the water, and is completely converted into caustic soda ; at a little interval, after the flame has ceased to burn, a globule of caustic soda, which has escaped solution, bursts and scatters in all directions ; the mouth of the bottle should always be covered to avoid the possible projection of particles of hot soda out of the bottle. The water in the bottle, tested with litmus paper, will be found to possess a strong alkaline reaction. If the bit of sodium be previously wrapped up in a piece of cloth, it will take fire in cold water or even on ice. The cloth prevents the sodium from moving about, and the heat of combination is therefore concentrated upon one spot.

Fig. 65.

373. **Sodium Hydrate** (**NaHO**). — When sodium is burnt upon water, a solution of **sodium hydrate** possessing an intensely alkaline reaction, remains behind ; but the hydrate is, in practice, made from the carbonate. The sodium carbonate is dissolved in boiling water, and slaked lime mixed with water to the consistency of cream is run into the hot liquor. The calcium of the slaked lime replaces the sodium in the sodium car-

bonate ; a white insoluble precipitate of calcium carbonate is formed, and sodium hydrate remains in the solution : $Na_2CO_3 + CaH_2O_2 = 2\,NaHO + CaCO_3$. The solution of sodium hydrate after separation from the precipitate of calcium carbonate is evaporated until it reaches the desired strength. The evaporation may be continued, until, at a nearly red heat, an oily liquid is obtained which solidifies on cooling to a white, somewhat translucent mass, whose composition corresponds to the formula **NaHO**. It is very soluble in water, and greedily absorbs both water and carbonic acid from the air.

374. **Caustic soda** is manufactured in large quantities principally for the use of the soap-maker. Soap, as we have already seen (**Exp. 111, § 243**), is made by boiling together grease or oil with caustic soda or potash ; soda-lye yields a hard soap, potash-lye a soft soap.

The cleansing action of soap, on which its use depends, may be explained as follows. When soap is dissolved in water it undergoes a chemical change ; regarding the soap as sodium stearate, we may say that a partial interchange takes place between the sodium of the soap and the hydrogen of the water, and there is formed a hydrogen sodium stearate and a certain amount of caustic soda. The caustic alkali thus set free attacks the greasy and oily matters of the article to be cleansed, and the somewhat sticky solution of soap holds in suspension, and thus removes mechanically the particles of dust and other insoluble matters.

375. **Sodium hydrate** is an example of the class of bodies called **bases** (§ 61). It colors litmus blue and turmeric brown, and when it is mixed in due proportion with an acid, a saline compound is formed which is neither acid nor alkaline, and which may bear no more resemblance to its proximate constituents than bread bears to flour and water, or rust to iron and oxygen.

From such reactions between acids and sodium hydrate, water is always disengaged simultaneously with the saline product, as may be illustrated by the following examples (compare also §§ 61 – 63): —

$NaHO$	+	HNO_3	=	$NaNO_3$	+	H_2O;
$2\,NaHO$	+	H_2SO_4	=	Na_2SO_4	+	$2\,H_2O$;
$NaHO$	+	$HC_2H_3O_2$ (Acetic acid.)	=	$NaC_2H_3O_2$ (Sodium acetate.)	+	H_2O.

While recognizing the frequent occurrence of such reactions as are thus represented between hydrated oxides, it must not be forgotten that many anhydrous saline compounds can be made by the direct combination, under appropriate conditions, of two oxides which contain no hydrogen. By heating one molecule of sodium hydrate, or 40 parts by weight, with one molecule, or 23 parts by weight, of sodium, an oxide of sodium (Na_2O) is obtained which contains no hydrogen; but this body has none of the properties described by the adjective alkaline, any more than the anhydrous teroxide of sulphur possesses the properties suggested to the mind by the term "**acid**." Now, the very same sodium sulphate which results from the second of the above reactions, may be prepared by bringing together this anhydrous sodium oxide and sulphuric anhydride: —

$$Na_2O + SO_3 = Na_2SO_4.$$

There exists another anhydrous oxide of sodium, corresponding in composition to the formula Na_2O_2, and the same sodium sulphate can be made by heating this oxide with sulphurous acid gas: —

$$Na_2O_2 + SO_2 = Na_2SO_4.$$

These facts show that a knowledge of the substances from which a salt may be made is not sufficient to establish any presumption concerning the molecular constitution of the salt itself.

376. **Sodium Biborate** or **Borax** ($Na_2B_4O_7, 10\,H_2O$). — **Borax** is a colorless, crystalline salt occurring ready formed in nature. The greater part of that used in the arts is prepared from the native boracic acid of Tuscany (§ **361**) by the addition of sodium carbonate. Carbonic acid is set free and the borax crystallizes out from the solution.

Borax has a feebly alkaline taste and reaction. When heated it bubbles up, loses its water, and melts below redness into a transparent glass; this glass dissolves many oxides of the metals, acquiring thereby various colors characteristic of these oxides. Hence borax is much used as a blowpipe test for determining the presence of certain oxides of the metals.

Exp. 177. — Make a little loop, about as large as this O, on the end of a bit of fine platinum-wire 6 or 8 c. m. long. Make the loop white-hot in the blowpipe flame, and thrust it while hot into some powdered borax; a quantity of borax will adhere to the hot wire; reheat the loop in the oxidizing flame; the borax will puff up at first,

and then fuse to a transparent glass. If enough borax to form a solid, transparent bead within the loop does not adhere to the hot wire the first time, the hot loop may be dipped a second time into the powdered borax. When a transparent glass has been formed within the loop of the platinum-wire, touch the bead of glass, while it is hot and soft, to a speck of manganese binoxide no bigger than the period of this type; reheat the bead with the adhering particle of oxide in the oxidizing flame; the black speck will gradually dissolve, and on looking through the bead towards the light, or a white wall, when the oxide has disappeared, the glass will be seen to have assumed a purplish-red color.

Fig. 66.

The same experiment may be performed with iron oxide, which imparts to the glass a yellow color, or with copper oxide, which imparts a bluish-green color. The oxidizing flame must be used in both these cases, as with the manganese oxide.

The power which borax possesses of dissolving metallic oxides suggests an explanation of its use in brazing and in soldering the precious metals. The solder will only adhere to a bright and clean metallic surface, and the borax which melts with the solder removes from the pieces of metal the film of oxide which would otherwise prevent the adhesion of the solder. Borax is also used by the assayer and refiner as a flux.

377. **Other Compounds of Sodium.** — **Sodium nitrate** ($NaNO_3$), a somewhat deliquescent and very soluble salt, occurs abundantly on the surface of the soil in certain desert districts of Peru. It is employed in the manufacture of nitric and sulphuric acids and as a manure. There are several phosphates of sodium corresponding to the different varieties of phosphoric acid. The most familiar of these phosphates, and the one commonly called sodium phosphate, is a crystallized salt of the formula $HNa_2PO_4,12\ H_2O$.

378. **Sodium Sulphide.** — Compounds of sodium and sulphur may be formed by heating sodium sulphate (Na_2SO_4) with charcoal; by heating sodium carbonate and sulphur together; and by boiling sulphur with caustic soda. There are at least

five different compounds (Na_2S, Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5) all soluble in water : when treated with an acid they all give off hydrogen sulphide (§ **117**) and from all except the first there falls a precipitate of finely divided sulphur, known as *milk of sulphur*. There is also a compound (**NaHS**) called sodium sulphydrate (hydrogen sodium sulphide) analogous in composition to sodium hydrate (**NaHO**).

Exp. 178. — Into a small flask put a pinch of flowers of sulphur and two teaspoonfuls of a solution of caustic soda. Boil the solution for some minutes ; the sulphur disappears and the liquid becomes dark colored. To the solution of sodium sulphide thus obtained, add dilute chlorhydric acid until the mixture turns litmus paper red ; observe the odor of hydrogen sulphide and also the precipitate of sulphur.

Fig. 67.

379. **Sodium silicates** may be prepared by dissolving silica in caustic soda, or by fusing together silica and sodium carbonate. The silicate of commerce called **water-glass** is of varying composition. Sodium silicate is an ingredient of common **glass,** as has already been seen. **Sodium hyposulphite** ($Na_2S_2O_3$, $5\,H_2O$), is a crystallized salt much used by photographers, because its aqueous solution is capable of dissolving silver chloride, bromide and iodide, — compounds much employed by the photographer, and very insoluble in water.

CHAPTER XX.

POTASSIUM (K).

380. The proximate sources of sodium compounds are the sea and salt springs and deposits. Potassium compounds, on the other hand, are derived indirectly from the soil. Arable soils are produced by the weathering and gradual decomposition of the common granitic rocks. These rocks contain a certain amount of potassium silicate ; the element **potassium** thus be-

comes a normal constituent of the earthy food of plants. No cheap and easy method has yet been devised for separating the potassium compounds from the other ingredients of the soil. Plants, however, are able to pick out and assimilate the potassium salts from the soil, so that by burning the plants and extracting the ashes with water a soluble potassium salt is obtained. The salt which is obtained from the ashes of plants by washing and evaporation is called **potash,** or, if refined, **pearlash,** and it is from this substance that the bulk of potassium compounds are obtained.

Exp. 179. — Place a handful of wood-ashes on a filter, and pour hot water over them, collecting the filtrate in a bottle and returning it upon the ashes two or three times, in order to obtain a stronger solution. To exhaust the ashes of their potash they must, of course, be treated with successive portions of hot water. This solution has a strong alkaline reaction upon test-paper. A few drops of it, poured into a test-tube containing a little dilute acid, occasion a brisk effervescence, a reaction from which we readily surmise the truth, that the potassium salt contained in the solution is potassium carbonate. By evaporating the rest of the solution to dryness in a porcelain dish, we obtain a small sample of crude potash.

Fig. 68.

381. **Potassium carbonate** (K_2CO_3) is a hygroscopic and very soluble salt. When exposed to damp air it becomes moist, and finally deliquesces. In this respect it does not resemble soda-ash, which is not hygroscopic, and is, for this reason among others, better adapted than potash for transportation, storing, and for most commercial uses.

Potassium carbonate was the most important source of alkali, until Leblanc's process made soda cheaper than potash. It is

still largely consumed in the manufacture of soap, glass, caustic potash and other compounds of potassium, but sodium salts have, to a great extent, displaced potassium salts in commerce and the arts.

382. **Hydrogen Potassium Carbonate** ($HKCO_3$). — This salt, which is commonly called "bicarbonate of potash" ($K_2O, H_2O, 2\,CO_2$), is prepared by passing a current of carbonic acid through a strong solution of potassium carbonate; crystals of the bicarbonate will be deposited, which are permanent in the air. **Saleratus** is properly potassium bicarbonate; but sodium bicarbonate is often substituted for it.

383. **Potassium Hydrate** (KHO). — The manufacture of potassium hydrate from potassium carbonate resembles, in every detail, the preparation of caustic soda from sodium carbonate (§ **373**). Potassium hydrate is a hard, whitish substance, possessing a peculiar odor and a very acrid taste. Like sodium hydrate, it rapidly absorbs moisture and carbonic acid from the air, and since the potassium carbonate thus formed is a deliquescent salt, this change will go on until the entire mass of hydrate is converted into a sirup of the carbonate; whereas, in the case of sodium hydrate, the absorption of water and carbonic acid is soon arrested by the formation of a coating of non-deliquescent sodium carbonate upon the surface of the lump of hydrate. Potassium hydrate, cast into small sticks, is employed by physicians as a cautery, — a use which illustrates forcibly its destructive effect upon animal and vegetable matters. Like sodium hydrate, its solution destroys ordinary paper, and cannot be filtered except through asbestos, or gun-cotton. A clear solution is best obtained by decantation from off the subsided impurities. In the chemical laboratory, solutions of caustic potash and caustic soda are in frequent use for absorbing acid gases, such as carbonic acid, and especially for separating the hydrates of other metals from solutions of their salts.

Exp. 180. — Dissolve a crystal of blue vitriol (copper sulphate) in a few cubic centimetres of cold water, and add to the solution

several drops of a solution of caustic potash. Copper hydrate is thrown down as a delicate, blue, insoluble precipitate, while colorless potassium sulphate remains in solution.

$$\underset{\text{Copper sulphate.}}{CuSO_4} + 2\,KHO = \underset{\text{Copper hydrate.}}{CuH_2O_2} + K_2SO_4.$$

384. **Potassium** (**K**). — This element, like sodium, is made from its carbonate by heating intensely a mixture of the carbonate and charcoal, in accordance with the reaction : —

$$K_2CO_3 + 2\,C = 2\,K + 3\,CO.$$

Potassium is a silver-white substance, of very brilliant lustre, which is brittle at 0°, soft as wax at ordinary temperatures, fuses at 62°.5, and is volatile at a red-heat. It is lighter than water, having a specific gravity of only 0.865. It is almost instantaneously oxidized by air and water at the ordinary temperature, and, when heated, by nearly every gas or liquid which contains oxygen. Like sodium, it must, therefore, be collected and kept under naphtha, out of contact with the air.

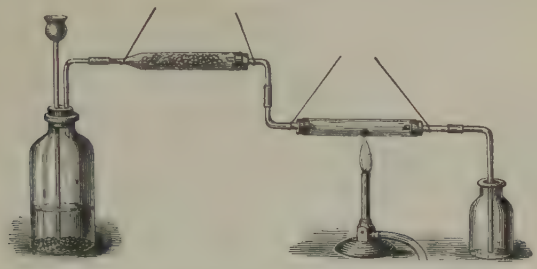
Exp. 181. — Throw a piece of potassium, as large as a small pea, upon some cold water in the bottom of a large bottle, and place a card or glass-plate over the mouth of the bottle. The potassium decomposes the water, and evolves heat enough to kindle the hydrogen which is given off; this hydrogen burns with a purplish-red color, imparted to the flame by a minute quantity of vaporized potassium. This color is characteristic of potassium compounds, as a yellow color is characteristic of sodium compounds. The water will have an alkaline reaction from the formation of potassium hydrate.

Fig. 69.

Exp. 182. — To a gas-bottle in which carbonic acid is being steadily evolved, according to Exp. 75, attach a chloride of calcium tube, and beyond this drying-tube a short tube of hard glass, from which an exit-tube leads into a small open bottle, as shown in Fig. 70. When the extinction of a lighted match in the open bottle proves the apparatus to be full of carbonic acid, thrust into the hard glass-tube a bit of potassium as big as a pea, previously dried between folds of blotting-paper, then gently heat the potassium with a lamp. The potassium will take fire and burn at the expense of the

oxygen of the carbonic acid, and black particles of carbon will be deposited upon the walls of the tube. After the reaction has ceased,

Fig. 70.



and the tube has been allowed to become cold, place it in a bottle of water, so that the saline mass (potassium carbonate) may dissolve ; the particles of carbon will then be seen more clearly, floating in the liquid ; they may be collected upon a filter. The reaction which has taken place may be thus expressed : —

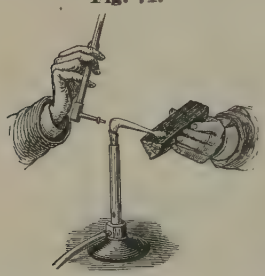
$$4\,K + 3\,CO_2 = 2\,K_2CO_3 + C.$$

385. **Potassium chloride** (**KCl**) is an important source of potassium compounds. It occurs in sea-water and in brine-springs ; it occurs also with other minerals in extensive deposits near Stassfurt in Germany. It resembles common salt in appearance and in taste ; it is somewhat more soluble in water and volatilizes at a lower temperature. **Potassium bromide** (**KBr**) and **iodide** (**KI**) resemble the chloride. They are much used in medicine, and the iodide is extensively employed by photographers.

386. **Potassium cyanide** (**KCN**) is a white, fusible, deliquescent solid which may be made by fusing nitrogenous organic matter with potassium carbonate or hydrate. It is of great use in galvanic gilding and silvering, since gold and silver cyanides are both soluble in a solution of potassium cyanide. Its solution dissolves silver sulphide, and has, therefore, been suggested for household use in cleaning silver-ware ; photographers sometimes use it for removing stains of silver nitrate from the hands ; but both these applications of potassium

cyanide are dangerous and inexpedient. The cyanide is intensely poisonous, not only when taken internally, but also when brought in contact with an abrasion of the skin, a cut or scratch. As a reducing agent, potassium cyanide has great power; it is especially useful in blowpipe reactions.

Fig. 71.



Exp. 183. — Scoop out a little hollow at one end of a bit of charcoal 8 to 12 c. m. long. Introduce into the hollow a mixture of equal parts of tin oxide (SnO_2), *dry* sodium carbonate and potassium cyanide. Heat with the reducing blowpipe-flame, for a minute or two. Metallic tin will be reduced

$$SnO_2 + 2\,KCy = Sn + 2\,KCyO$$ (potassium cyanate).

387. **Potassium Ferrocyanide** (K_4FeCy_6). — When potassium carbonate is fused with nitrogenous organic matter potassium cyanide is formed, as has been stated in the preceding section. When this fusion takes place in the presence of iron (as iron filings, for instance), the fused mass treated with water yields a solution of a salt known as **potassium ferrocyanide.** This salt crystallizes in large yellow crystals, and is met with in commerce under the name of "yellow prussiate of potash" nearly in a state of purity.

Potassium ferrocyanide is a salt of an acid called **ferro-cyanhydric acid** (H_4FeCy_6), a compound of hydrogen with the hypothetical quadrivalent radical **ferro-cyanogen, $FeCy_6$**, or **Fcy**. When potassium ferrocyanide is heated with sulphuric acid, it is decomposed in accordance with the reaction: —

Potassium ferrocyanide.			Water.		Sulphuric acid.
$K_4FeC_6N_6, 3\,H_2O$	+	$3\,H_2O$	+	$6\,H_2SO_4$	
$= 6\,CO$	+	$2\,K_2SO_4$	+	$FeSO_4$	+ $3\,(NH_4)_2SO_4$.
Carbon protoxide.		Potassium sulphate.		Iron sulphate.	Ammonium sulphate.

This reaction has already been taken advantage of in the preparation of carbon protoxide (Exp. 81, § 195).

388. **Potassium Ferricyanide** (K_3FeCy_6). — When a current of chlorine gas is passed through a solution of ferrocyanide of

potassium the following reaction takes place : — $K_4FeCy_6 + Cl = K_3FeCy_6 + KCl$. The compound K_3FeCy_6, potassium ferricyanide, may be obtained in beautiful deep-red crystals by evaporating the solution. This compound is known in commerce as "red prussiate of potash."

Potassium ferricyanide is a salt of **ferri - cyanhydric acid** (H_3FeCy_6), a compound of hydrogen with the hypothetical trivalent radical, $FeCy_6$ or **Fdcy**. The ferro- and ferri-cyanides of potassium afford valuable means of identifying **iron** in its compounds, as will be seen in § 477.

389. **Potassium sulphate** (K_2SO_4) differs from sodium sulphate in crystallizing as an anhydrous salt. The salt enters into the composition of many of the double sulphates which are called **alums**, from the name of the commonest member of the class, the aluminum and potassium sulphate.

390. **Hydrogen Potassium Sulphate** ($HKSO_4$). — This salt, commonly called the "bisulphate," is formed on a large scale as a residuary product, whenever nitric acid is manufactured from potassium nitrate. When ignited, sulphuric acid is given off and potassium sulphate remains : —

$$2\,(HKSO_4) = K_2SO_4 + H_2SO_4.$$

391. **Potassium Nitrate** (KNO_3). — This valuable salt, commonly called saltpetre, or nitre, is very widely diffused in nature. In many localities, it is found in caverns or caves in calcareous formations, but the chief commercial source of the salt is the soil of tropical regions, especially of districts in Arabia, Persia, and India, where the nitrate is found as an efflorescence upon the surface of the ground, or in the upper portion of the soil itself. The saltpetre is extracted by treating the earth with water, and obtained in an impure state by evaporating the solution. The crude product is purified by successive recrystallizations.

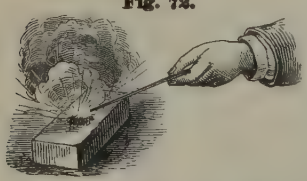
This natural production of nitrates appears to result mainly from the putrefaction of vegetable and animal matters, in presence of the air and of alkaline or earthy bases capable of fixing the nitric acid as soon as formed. The well-waters of towns, contaminated by neighboring sewers or cesspools, nearly always contain nitrates. Nitrates are seldom wholly wanting in a fertile soil, or in spring or river water.

The process of *nitrification* seems to be brought about by an organized ferment which lives in vegetable mould. We have seen that the yeast plant accomplishes the conversion of sugar into alcohol (§ 225); something similar is supposed to take place in nitrification.

392. **Potassium nitrate** is white, inodorous and anhydrous, and has a cooling, bitter taste. When pure, it is permanent in the air, — a fact of great importance, inasmuch as the chief use of this salt is in the manufacture of gunpowder. Were it hygroscopic, like sodium nitrate, it would not be applicable to this use. It is very soluble in water, especially in hot water; it melts below a red heat to a colorless liquid without loss of substance, but at a red heat it gives off oxygen, and suffers decomposition. Its most marked chemical characteristic is its **oxidizing power.**

Exp. 184. — Mix 5 grms. of powdered saltpetre with 1 grm. of dry, powdered charcoal; place the mixture on a piece of porcelain and ignite it with a hot wire. When the deflagration is over, a white solid will be found upon the porcelain. Dissolve this solid in a few drops of water; the solution will be alkaline to test-paper; add a few drops of a dilute acid; a brisk effervescence marks the escape of carbonic acid. The nitrate has oxidized the carbon to carbonic acid, part of which escaped with the nitrogen during the deflagration, while part entered into combination with the potassium: — $4\ KNO_3 + 5\ C = 2\ K_2CO_3 + 3\ CO_2 + 4\ N$.

Fig. 72.



Gunpowder is an intimate mechanical mixture of soft-wood charcoal, sulphur and potassium nitrate, in the proportions of 70 or 80 per cent of the nitrate to 10 or 12 per cent of each of the other ingredients. When gunpowder burns in a closed space, the reaction that takes place is quite complex; speaking in general terms, however, we may say that the oxygen of the nitrate combines with the carbon to form carbonic acid and carbonic oxide, while the sulphur is retained by the potassium, and nitrogen is left free. A very large proportion of gas, as compared with the bulk of the solid powder, is thus evolved when powder is burned. Moreover gunpowder burns rapidly and with great evolution of heat, so that the volume of gas, large at

any temperature, is enormously expanded at the moment of its formation; hence it happens that the gas set free may be capable of occupying a thousand or fifteen hundred times as much space as the powder which generated it. An enormous pressure is thus engendered at the spot where the powder burns, and to this pressure some part of the matter which confines the powder must yield. In the case of fire-arms it is the ball which yields to the pressure: in blasting it is the solid rock itself that is torn apart.

393. **Potassium chlorate** ($KClO_3$) is a white, crystallized salt much used in medicine, in calico-printing, in pyrotechny, in the match-manufacture and in the chemical laboratory, on account of its large oxygen contents. It is an oxidizing agent of the most vigorous description. At a red heat it is resolved into potassium chloride and oxygen (**Exp. 4**):—

$$KClO_3 = KCl + 3\,O.$$

Potassium chlorate is so prompt an oxidizing agent that mixtures of it with combustible bodies often detonate violently when struck or heated. These combustions are attended with great danger unless very small quantities be used.

Exp. 185. — Provide a bit of ordinary phosphorus, as large as a pin's head; add enough finely powdered potassium chlorate to cover the phosphorus; fold the mixture tightly in a small piece of writing-paper; place the parcel upon an anvil and strike it sharply with a hammer. The mixture will explode with violence.

Strong acids like sulphuric, nitric and chlorhydric acids, decompose potassium chlorate with evolution of oxides of chlorine, or of chlorine and oxygen. The decomposition is often attended with decrepitation, and sometimes with a flashing light; combustibles, like sulphur, phosphorus, sugar and resin, are inflamed by the gases evolved.

Exp. 186. — Pour into a conical test-glass 25–30 c. c. of water, and throw into the water some scraps of phosphorus, weighing together not more than 0.3 grm., and 3–4 grms. of crystals of potassium chlorate. By means of a thistle-tube bring 5 or 6 c. c. of strong sulphuric acid into immediate contact with the chlorate at the bottom of the glass. Then withdraw the thistle-tube. In a moment the

phosphorus is kindled, and burns with vivid flashes of light beneath the water. An evolution of chlorine accompanies the reaction.

Exp. 187. — Rub 4 or 5 grms. of clean potassium chlorate, free from dust, to a fine powder in a porcelain mortar. In powdering potassium chlorate, care must be taken that the mortar and pestle are perfectly clean, and the salt is free from organic matter, and violent percussion and heavy pressure upon the contents of the mortar must be wholly avoided. Place the powdered chlorate on a piece of paper, add an equal bulk of dry, powdered sugar to the pile, and with the fingers and a piece of card, mix the two materials thoroughly together. Mixtures of potassium chlorate and organic matter are liable to explode, if strongly rubbed or but lightly struck. Wrap the mixture in a paper cylinder, and place the cylinder on a brick in a strong draught of air ; let fall upon the mixture a drop of sulphuric acid from the end of a glass rod ; a very vivid combustion will ensue, with the violet-colored flame characteristic of potassium.

394. **Potassium tartrate** ($K_2C_4H_4O_6$) is a very soluble crystalline salt ; the hydrogen potassium tartrate ($HKC_4H_4O_6$), known in the crude state as "argol," and when purified as "cream of tartar," has already been described in § **327.**

CHAPTER XXI.

AMMONIUM SALTS.

395. By neutralizing an aqueous solution of ammonia with nitric acid there is formed, in accordance with the reaction $NH_3,H_2O + HNO_3 = (NH_4)NO_3 + H_2O$, a body, $(NH_4)NO_3$, corresponding in composition to potassium nitrate (KNO_3) except that the group of atoms NH_4 takes the place of the atom **K**. If we had used chlorhydric acid there would have been formed a body, NH_4Cl, corresponding to potassium chloride, KCl; sulphuric acid would give $(NH_4)_2SO_4$ corresponding to K_2SO_4. To explain the constitution of these and similar salts, the group of atoms NH_4 is regarded as playing the part of a

metallic element, like sodium or potassium, and has received the name **ammonium**. We have, however, no positive evidence of the separate existence and metallic character of this group of atoms NH_4.

All ammonium salts, whether solid or in solution, evolve ammonia-gas (NH_3) when heated with the hydrates of sodium, potassium, calcium and a few other metals.

Exp. 188.—To a few cubic centimetres of a solution of ammonium chloride in a test-tube, add a few drops of a solution of caustic soda, and boil the liquid. The gaseous ammonia can be detected by its odor. If in any case the ammonia evolved be in so small a quantity that its characteristic smell cannot be detected, it may be recognized by its property of restoring the blue color to reddened litmus paper (§ 60), and of forming white fumes by contact with a rod moistened with somewhat dilute chlorhydric acid. The reaction may be formulated as follows: —

$$NH_4Cl + NaHO = NaCl + NH_3 + H_2O.$$

396. The solution of ammonia-gas in water (NH_3,H_2O) may be regarded as a solution of ammonium hydrate, $(NH_4)HO$, comparable with the solution of caustic soda, $NaHO$, or caustic potash, KHO. This solution produces, indeed, many of the effects which the solutions of the caustic alkalies produce; it neutralizes acids, and sets free the hydrates of many metals from solutions of their salts; it is capable of saponifying fats (§ **243**) and is, in short, a powerful **base.**

Exp 189.— Dissolve a small crystal of alum in 6–8 c. c. of water in a test-tube and add ammonia-water until the solution, after being well shaken, smells strongly of ammonia. A gelatinous precipitate of aluminum hydrate will appear in the liquid.

Ammonium salts are very numerous, but only the few which are of present importance in the useful arts will be here described.

397. **Ammonium Chloride** (NH_4Cl). — This salt, commonly called sal-ammoniac, is found native in many volcanic regions.

The commercial supply of the salt was formerly obtained from the soot resulting from the incomplete combustion of camels' dung. The

raw material, whence ammonium salts are now manufactured, is derived from gas-works and bone-black factories. Coal and bones contain a portion of nitrogen which, during the process of distillation, is partially converted into ammonia (§ 68); this ammonia combines with the carbonic acid and sulphuretted hydrogen, which are likewise products of the distillation, and these compounds are condensed into a somewhat watery liquor, contaminated with tarry and oily matters, from which the ammonium salts are subsequently extracted.

Ammonium chloride serves for the preparation of ammonia (**Exp. 27**), and of ammonium carbonate. It is somewhat employed in dyeing, and also in certain processes with metals, such as tinning, soldering and silvering copper and brass, and galvanizing (zincing) iron. When heated, it sublimes much below redness, without undergoing fusion.

Exp. 190. — Heat a bit of sal-ammoniac on a piece of porcelain, and observe the low temperature at which the solid is completely converted into vapor.

398. **Ammonium sulphate** ($(NH_4)_2SO_4$) is a colorless, crystalline salt resembling potassium sulphate. It is employed in the manufacture of ammonium alum, as an ingredient of artificial manures, and as a source of other ammonium salts.

399. **Ammonium Nitrate** ($(NH_4)NO_3$). — The method of preparing this salt, and its complete decomposition by heat, have been already described (see **Exp. 17, § 47 and § 67**). The salt crystallizes in long needles; it has a pungent taste, is very soluble in water, and, in dissolving, produces sharp cold.

400. **Ammonium Carbonates.** — The commercial carbonate (*sal-volatile*) is a white, semi-transparent, fibrous substance, with a pungent taste and a strong ammoniacal smell; it is prepared, on a large scale, by the dry distillation of bones, horn and other animal matters. The product is purified from empyreumatic substances by repeated sublimation. Ammonium carbonate may also be obtained by heating the chloride (or sulphate) with calcium carbonate; the ammonium carbonate sublimes, leaving a residue of calcium chloride (or sulphate). There are several ammonium carbonates; the most permanent is the "bicarbonate" or hydrogen ammonium carbonate

($H(NH_4)CO_3$). Into this the commercial carbonate which is an impure product gradually changes.

401. The **sulphides** of ammonium correspond to those of sodium (§ **378**); a solution of the **sulphydrate** (NH_4HS) which is colorless when fresh, but gradually becomes yellow owing to the formation of higher sulphides, is much used in the analytical laboratory.

402. **Isomorphism.** — The resemblance of the salts of ammonium to those of potassium is rendered more striking from the fact, that in many cases it is true of corresponding salts, that the crystalline form of the two bodies, as well as their texture, color and lustre, is identical. If solutions of these two salts be mixed, neither of the salts can subsequently be crystallized out by itself, when the solution is evaporated; the crystals obtained will be composed of the two salts mixed in the most varied proportions. Bodies which are thus capable of crystallizing together in all proportions, without alteration of the crystalline form, are said to be **isomorphous** (*like-formed*).

CHAPTER XXII.

LITHIUM, RUBIDIUM, CÆSIUM AND THALLIUM.

SPECTRUM ANALYSIS.

403. **Lithium** (**Li**). — This rare metal occurs as a constituent of not a few minerals, especially micas and feldspars, but does not form a large percentage of any of them. In very small proportion, it has been recognized in sea-water, mineral-waters and almost all spring-waters, in milk, tobacco and human blood. It is a widely-diffused, but not abundant substance.

Metallic lithium resembles sodium and potassium. It is the lightest of all known solids which include no air, its specific gravity being only 0.59. The atomic weight of the element

is also low; namely, 7. In its chemical relations, lithium closely resembles sodium and potassium, but is somewhat less energetic.

All the volatile lithium compounds color a gas-, alcohol- or blowpipe-flame carmine-red. The most delicate reaction for the detection of lithium, the test which has revealed its existence in a great variety of substances which were never imagined to contain it, is the presence of one bright line, of a peculiar red, in the **spectrum,** seen on looking through a glass prism at a flame colored with a lithium compound.

404. **Spectrum Analysis.** — We have had occasion to observe that certain chemical substances, like boracic acid and salts of sodium, potassium and lithium, impart peculiar colors to the blowpipe flame, or to any other hot and colorless flame. If these colored flames are looked at through a prism, a narrow pencil of the colored light being directed through a slit upon the prism, it will be seen that each different flame produces a peculiar **spectrum,** consisting of one or more distinct bright lines of colored light and bearing no resemblance to the continuous band of rainbow-colors which constitutes the common spectrum produced by a pencil from any source of white light. Thus, the spectrum of the yellow sodium flame consists of a single, bright, yellow line; the purple potassium flame gives a spectrum containing two bright lines, one lying at the extreme red and the other at the extreme violet end, and another, fainter red line; while the lithium spectrum consists of a very characteristic red line and a fainter orange line.

The peculiar lines which characterize the spectrum of any element are invariably produced by that element, and never by any other substance, and not only the color and number of lines, but their position in the normal spectrum, always remain unaltered. When the spectrum of a flame colored with a mixture of sodium and potassium salts is examined, the yellow line of sodium is seen in its place, and the red and purple lines of potassium are as visible in their respective positions as if no sodium had been present. This example illustrates

one great advantage which the use of the prism gives, — the unaided eye cannot distinguish the potassium color in the presence of the intense sodium-yellow, the brighter color hiding the paler; but with the prism it is easy to detect each of several ingredients of a mixture by the appearance of its characteristic lines.

A new method of analysis, of extreme delicacy, is based upon these facts. **Spectrum analysis** is competent to detect the $\frac{1}{2,736,000,000}$ of a gramme of sodium, or the $\frac{1}{60,000,000}$ of a gramme of lithium, and many other elements in incredibly small proportions. So extreme is the delicacy of the method, that it brings into plain sight minute quantities which altogether escape the coarser process of analysis, and reveals, as substances common in familiar things, elements which were long supposed to be of extreme rarity. Thus, the presence of lithium, formerly considered a rare element peculiar to a few obscure minerals, has been demonstrated by spectrum analysis in many drinking-waters, in tea, tobacco, milk and blood. A still more striking illustration of the value of spectrum analysis is to be found in the discovery of a number of new elementary bodies by its means; among these elements are **rubidium, cæsium, thallium, indium,** and **gallium.**

The methods and processes of spectrum analysis are not applicable to colored artificial lights alone; they have been applied with encouraging success to the lights of various quality which emanate from the sun, the stars and the nebulæ; but the details of these observations belong rather to physics than to chemistry.

405. **Rubidium and Cæsium** (**Rb** and **Cs**). — These two elements are always found together, and in association with potassium. Though extensively diffused, they generally occur in very minute quantities. **Rubidium** seems to be rather the more abundant. Ten kilogrammes of the mineral water in which these metals were first discovered yield not quite two milligrammes of cæsium chloride, and about two and a half milligrammes of rubidium chloride. The properties of both

rubidium and cæsium differ from those of sodium and potassium, not in kind but only in degree. They are therefore classed with sodium and potassium as **alkali-metals.** The atomic weight of rubidium is 85.7, of cæsium 133.

406. **Thallium** (Tl). — Thallium is a malleable, ductile metal resembling lead in external characters. It is found in certain varieties of iron pyrites. The properties of thallium are intermediate between those of lead and those of sodium and potassium. Like the alkali-metals, it replaces hydrogen atom for atom; its atomic weight is 204.

CHAPTER XXIII.

SILVER (Ag) — THE ALKALI-METALS.

407. **Silver** is a widely-diffused and quite abundant element, but in its mode of occurrence it differs widely from the **alkali-metals** which we have just been studying. In the first place, it frequently occurs native, both pure, and alloyed with mercury, copper and gold, — a mode of occurrence quite impossible for the alkali-metals, because of their readiness to combine with the elements of air and water. The metal more commonly occurs in combination with sulphur, mixed with sulphides of lead, antimony, copper and iron. It is from argentiferous sulphides that the larger part of the silver of commerce is extracted, and, among ores of this kind, the argentiferous lead sulphide (galena) is the most abundant. Combinations of silver with selenium, tellurium, chlorine, bromine and iodine are also to be enumerated among silver-containing minerals; of these the chloride (horn-silver) occurs in quantities large enough to make it valuable as an ore of the metal. It is noticeable, that the only elements which are extracted in any quantity from their chlorides as ores, are sodium, potassium and silver. A small proportion of silver

exists in sea-water (about 1 milligramme in 100 litres), and its presence has been recognized in common salt, in chemical products in the making of which salt is used, in various sea-weeds, in the ashes of land-plants, in the ash of ox-blood, and probably also in coal. In sea-water it exists, as sodium and potassium do, in the form of chloride.

408. **Silver** (**Ag**). — The element **silver** is much more familiarly known than any of its compounds: known from the earliest ages, this metal has always been prized as much for its beauty as for its rarity. White, brilliantly lustrous, susceptible of an admirable polish, wonderfully malleable and ductile, the best known conductor of heat and electricity, fusible only at a very elevated temperature, and permanent in the air, whether hot or cold, wet or dry, it represents and embodies in the completest sense all that is commonly understood by the term **metal.**

This word **metal** cannot be strictly defined; it is a conventional term, vaguely used because expressing a vague idea. Thus metals would all be solid were not mercury, and perhaps cæsium, fluid; they are generally heavy, but lithium, sodium and potassium float upon water: they have all a peculiar lustre, called metallic; but this lustre does not characterize metals alone, for coke and graphite, galena, molybdenite, and many other minerals often exhibit a similar lustre; they may all be said to be opaque, but gold may be beaten out so thin as to transmit a greenish light. While it is not possible to define the term **metal** with precision from **chemical,** any more than from **physical** properties, one general chemical fact deserves attention in this connection; — the so-called **non-metallic elements** unite with oxygen and hydrogen to form **acids;** while the **metallic elements** unite with oxygen and hydrogen to form **bases.** This general fact, however, does not give a sharp line of demarcation, as some elements form both acids and bases; thus in the case of arsenic, while there is an **arsenic terchloride,** there are also **arsenites** and **arseniates** of various metals. In the table on page 256 the elements preceding **gold** are those usually

known as non-metallic : those which follow are the metallic elements.

409. **Silver** combines slowly with chlorine, bromine and iodine, and promptly with sulphur. The tarnishing of silver is due to the formation of a thin film of the black sulphide over the metallic surface, by combination between the silver and the sulphur of the sulphuretted hydrogen which is often present in the air of towns and houses. The specific gravity of silver is 10.5, and its atomic weight 108.

410. The physical and chemical qualities of silver fit it to serve as a medium of exchange, and as the material of jewelry and plate. But as the pure metal would be rather too soft for ordinary use, it is hardened by combining with it a small proportion of copper. The proportion of copper in the "standard" silver employed for coinage varies in different countries : — in the United States and in France it is 10 per cent ; in Great Britain it is 7.5 per cent ; in Germany it is 25 per cent.

Exp. 191. — Place one or two dimes in a small flask, and cover them with nitric acid diluted with two parts of water. Warm the flask gently in a place where there is a good draught of air ; the coins will gradually dissolve, with evolution of a gas, nitric oxide, which, on contact with air, produces the abundant red fumes which escape from the flask ; add more nitric acid, from time to time, if necessary to complete the solution. The blue solution contains both the silver and the copper dissolved in nitric acid.

Place in the blue solution two or three copper coins, and leave the flask at rest for some days in a warm place. Then collect the little plates of pure silver, which have separated from the solution, upon a filter, and wash them, first with water, and then with ammonia-water, until the ammonia-water no longer shows any tinge of blue. This silver, washed finally with water and dried, is wellnigh pure ; if it be again dissolved in nitric acid, the solution will contain nearly pure silver nitrate.

411. **Silver Nitrate** ($AgNO_3$). — This salt, as we have already seen, is obtained in solution by dissolving silver in nitric acid. When such a solution is evaporated to the point of crys-

tallization, the nitrate is obtained in transparent, anhydrous, tabular crystals, which are soluble in their own weight of cold water, and in half their weight of hot water. The fused salt is used in surgery as a caustic, under the name of **lunar caustic.**

Silver nitrate, when pure, is not altered by exposure to sunlight ; but if it be in contact with organic matter, light readily decomposes it, and a black, insoluble product is formed of no ordinary stability. Hence the solution of the nitrate stains the skin black, and the salt forms the basis of an **indelible ink** used for marking linen and other fabrics. Silver nitrate is much used in photography.

412. **Silver chloride** (**AgCl**) occurs native sometimes in cubical crystals and sometimes in compact, semi-transparent masses, which, from their general appearance, have given the mineral the name of **horn-silver.** Silver chloride may be precipitated from any soluble silver salt by adding to the silver solution chlorhydric acid, or the solution of any soluble chloride. Silver chloride is insoluble in water and acids, but is dissolved by ammonia-water. Exposed to the light, it is partly decomposed and becomes dark colored. **Silver iodide** and **bromide** are prepared by adding a solution of a soluble iodide or bromide, to a solution of some silver salt.

Exp. 192. — Fill three test-tubes one-third full of water, and pour into each a few drops of a moderately strong solution of silver nitrate. Add to the first test-tube 2 or 3 c. c. of a solution of sodium chloride, and shake the tube violently ; a dense, white, curdy precipitate of the silver chloride will be produced. Add to the second test-tube 2 or 3 c. c. of a solution of potassium bromide, and shake the tube ; a yellowish precipitate of silver bromide will be thrown down. Add to the third test-tube 1 or 2 c. c. of a solution of potassium iodide, and shake up the liquid ; a pale-yellow flocculent deposit of silver iodide will be formed.

Withdraw from each test-tube a portion of the precipitate it contains, and try to dissolve each precipitate in moderately strong nitric acid ; the attempt will fail, for these silver salts are insoluble in nitric acid.

Withdraw from each test-tube another portion of the precipitate it

contains, and treat each precipitate with ammonia-water; the silver chloride will dissolve easily, the bromide less easily, the iodide with difficulty. Lastly, pour upon the remnants of the original precipitates in the three test-tubes a moderately strong solution of sodium hyposulphite; all three precipitates will immediately dissolve.

Exp. 193. — Precipitate some curdy silver chloride by adding sodium chloride solution, or chlorhydric acid, to a solution of silver nitrate, so long as any precipitate is produced. Throw the precipitate upon a filter, and wash it with water; then open the filter, spread the chloride evenly over it, and place it in direct sunlight. The white precipitate rapidly changes to violet on exposure to the sun's rays, the depth of shade increasing as the action of the light continues. Upon the facts illustrated in this and the preceding experiments the main processes of photography depend.

413. **Other Silver Compounds.** — **Silver oxide** (Ag_2O) corresponds to sodium oxide (Na_2O). It is decomposed below a red heat, giving up its oxygen. The hydrate **AgHO** is very slightly soluble in water giving an alkaline reaction. At 60° it is converted into the oxide (Ag_2O).

Silver cyanide (**AgCN**) is a white powder insoluble in water. It is soluble in potassium cyanide, and so dissolved is used in electro-plating. **Silver sulphide** (Ag_2S) occurs as a native mineral. **Silver sulphate** (Ag_2SO_4) is formed when metallic silver is boiled with strong sulphuric acid. The reaction which takes place is: —

$$2\,Ag + 2\,H_2SO_4 = Ag_2SO_4 + 2\,H_2O + SO_2.$$

414. **Photography.** — The chemical changes which the salts of silver undergo, when exposed to light, are the basis of the art of photography, not because these are the only salts which are affected by light, but because none are so advantageous, on the whole.

In order to get a photograph upon glass, a transparent film capable of holding the necessary silver salt must first be attached to the glass plate. *Collodion*, a solution of a variety of gun-cotton in a mixture of alcohol and ether, is the material of this film. To the collodion is added a solution of potassium, cadmium or ammonium iodide, or a mixture of these salts.

The collodion thus prepared is poured rapidly over a clean and dry surface of plate-glass; the volatile solvents evaporate rapidly, and as

soon as the film is coherent, the glass is allowed to remain for several minutes in a bath of silver nitrate, very slightly acidified with acetic or dilute nitric acid. A yellow layer of silver iodide is produced in the film, and potassium, cadmium or ammonium nitrate dissolves in the bath. The plate is then exposed in the camera for a few seconds. When removed, no image is perceptible ; but on pouring over the film a solution of gallic or pyrogallic acid in alcohol and acetic acid, or a solution of ferrous sulphate mixed with a few drops of a weak solution of silver nitrate, the image will be developed, slowly or rapidly, according to the nature and strength of the developing liquid, the degree of exposure, and the intensity of the light. The illuminated portions of the picture will appear, under the action of the *developer*, more or less black, while the shaded portions will retain the yellow color of the iodide. As soon as the details of the shaded portions appear, the liquid is washed off and the development arrested. A saturated solution of sodium hyposulphite is then poured over the film to dissolve off the yellow silver iodide where it has not been affected by the light ; only the reduced portions of silver remain, and they appear more or less opaque. The plate must finally be very thoroughly washed to remove all traces of the hyposulphite, and then dried and varnished on the collodion side to protect the film from injury.

From the glass "negative" thus produced, "positive" pictures on paper may be printed. The paper is floated for five minutes on a solution of sodium or ammonium chloride ; when dried, it is floated in a dark room, for five minutes, on its salted surface, in a solution of silver nitrate, and again dried. To produce the positive picture, the paper is exposed to light under the negative to be copied, until the lights of the picture are of a pale lilac hue, and the shades of a deep bronze color. After being thoroughly washed, the paper is transferred to a "toning" bath, which consists of a very dilute solution of hydrogen sodium carbonate ("bicarbonate of soda") with a minute proportion of gold chloride. The picture is kept in motion while in this bath ; it remains there until its shades have acquired a deep purple-black color. It is only in those parts of the picture in which the silver has been well reduced that this toning effect is produced. The picture is again washed in water, and soaked for fifteen minutes in a solution of sodium hyposulphite, in order to remove all the silver chloride which is contained in the substance of the paper. Finally, the picture must be soaked for twenty-four hours in water which is constantly renewed, in order to wash away every trace of the com-

pound sodium and silver hyposulphite. No photograph will keep long, unless the silver chloride has been completely dissolved by the hyposulphite, and the compound hyposulphite washed away with a thoroughness that leaves no trace behind. If the first condition is not fulfilled, diffused daylight will alter the picture; if the second condition is not complied with, yellow or brown stains will ultimately destroy the picture.

As in every other art which embraces many details, and demands a trained eye and hand, eminent skill in photography can, as a rule, be acquired only by long practice.

415. **The Alkali Group.** — The metals which must plainly be classed together under this head are sodium, potassium, (ammonium), lithium, rubidium and cæsium. Two other metals are better classed with this group than elsewhere, but their likeness to the alkali-metals is but partial, and in many respects their properties are quite unlike those of the six metals just enumerated; these two metals are silver and thallium. The common properties of the alkali-metals are mainly these; — they have the lustre of silver, are soft, easily fusible, and volatile at high temperatures; they unite greedily with oxygen, and decompose water with facility, forming basic hydrates which are very caustic and intensely alkaline bodies, not to be decomposed by heat; their carbonates, sulphates, sulphides and chlorides, and indeed the vast majority of their salts, are soluble in water, and each metal forms but one chloride, one bromide and one iodide; they all form basic hydrates, and never an acid hydrate; they occur in nature in modes analogous, though not the same; their corresponding salts are often, though not always, isomorphous; lastly, there is a general, though not absolute, uniformity among the formulæ of the compounds into which these elements enter; so that, if a compound of a given composition is proved to exist for one of these elements, the strong presumption is that analogous compounds with all the other elements of the group exist likewise with properties similar, though not identical.

Silver and thallium present, on the whole, so few points of resemblance to the alkali metals that they would not be comprehended in the same group with them were it not for one

consideration weighty enough to turn the balance when the discussion of other properties leaves the matter in doubt. Sodium, potassium (ammonium), lithium, cæsium, rubidium, silver and thallium all replace hydrogen, atom for atom. All these elements are exchangeable for hydrogen and with each other, atom for atom, and in the present state of the science they must be regarded as the only metals thus equivalent to hydrogen. The atoms of the elements of the chlorine group, including fluorine in that designation, and of the seven elements above enumerated, are exchangeable for the same number of atoms of hydrogen; each atom is *worth one* in exchange, and these elements are therefore said to be **univalent** (see § **74**).

CHAPTER XXIV.

CALCIUM, STRONTIUM, BARIUM AND LEAD.

CALCIUM (Ca).

416. The metal **calcium** is a constituent of several of the commonest and most important minerals; it forms a very considerable portion — perhaps as much as one-sixteenth — of the solid crust of the earth. The metal itself is yellowish-white, lustrous and ductile, and suffers no change in dry air at the ordinary temperature. In moist air it oxidizes quickly, and it decomposes water with evolution of hydrogen. At a red heat it melts, and, if oxygen be present, takes fire and burns with a bright light. It is a **bivalent** element; its atomic weight is 40.

417. **Calcium carbonate** ($CaCO_3$) occurs in nature in many different forms, sometimes finely crystallized, sometimes in an amorphous condition. Limestone, chalk, marble, calc-spar and coral are calcium carbonate: the shells of shell-fish are almost

entirely composed of it, and it is an important constituent of dolomite, marl and many other rocks and minerals.

In all its varieties calcium carbonate is readily attacked by acids, even if these be dilute ; the action is attended with effervescence, owing to the expulsion of carbonic acid and the escape of this gas through the liquid : —

$$CaCO_3 + 2\,HCl = CaCl_2 + CO_2 + H_2O.$$

418. **Calcium carbonate,** though tasteless, is slightly soluble in water, and the solution exhibits a faint alkaline reaction ; it is, however, rather freely soluble in water charged with carbonic acid (§ **192**).

Exp. 194. — Place in a test-tube 20 or 30 drops of lime-water, and as much pure water ; in the mixture, immerse the delivery-tube of a bottle from which carbonic acid gas is being evolved (Exp. 75). Calcium carbonate will be thrown down at first, but after a while, as the water in the test-tube becomes saturated with carbonic acid, the precipitated carbonate will re-dissolve, and there will be obtained a perfectly clear solution, which, in spite of the large proportion of carbonic acid contained in it, has a decided alkaline reaction. By boiling the solution, so that a portion of its carbonic acid may be expelled, the calcium carbonate can be again precipitated. So, too, if the liquid be left exposed to the air, it will gradually give off carbonic acid, and become turbid from deposition of calcium carbonate.

To the solubility of calcium carbonate in water containing carbonic acid, and to the fact that on the escape of the carbonic acid the calcium carbonate is deposited, is due the formation of calcareous petrifactions, of stalactites and stalagmites, of the stones called tufa and travertine, and of many deposits of crystallized calcium carbonate. Whenever water, charged with calcium carbonate, flows out from the earth into the open air, or trickles into hollows or caverns within the earth, carbonic acid is given off in the gaseous state, and calcium carbonate is deposited. Stalactites are the pendent masses, like icicles, which hang from the roofs of caverns, and the walls of cellars, bridges and like covered ways ; stalagmites are the opposite masses which grow up out of the drops of water which fall from the stalactites above them, before all the carbonate has been deposited.

419. **Calcium Oxide** (**CaO**). — On being heated, calcium carbonate begins to give off carbonic acid at a low red heat,

and at full redness is completely resolved into calcium oxide, commonly called **quick-lime**, and carbonic acid. For use in the arts, limestone is burned in special furnaces, of peculiar construction, called lime-kilns, some of which are so arranged that they may be kept in operation for years without intermission.

Calcium oxide is infusible at the most intense heat at our present command, and is, therefore, used for making crucibles in which the most refractory metals are melted by the aid of the compound blowpipe.

420. **Calcium Hydrate** (CaH_2O_2). — When water is brought in contact with calcium oxide, the latter swells up and falls to powder; a large amount of heat is evolved, and there is obtained a compound of calcium, hydrogen and oxygen, commonly called slaked lime, or in chemical language **calcium hydrate**: — $CaO + H_2O = CaH_2O_2$.

Exp. 195. — Place a lump of recently-burned quick-lime, weighing about 30 grms., upon a large earthen plate; pour upon the lime some 15 or 20 c. c. of water, and observe how much the lime increases in bulk as it is converted into calcium hydrate. The heat of the mass may be shown by thrusting an ordinary friction-match into the middle of it; inflammation will ensue.

So much heat is developed during the union of water with lime, that wood will quickly be brought to the kindling temperature and inflamed, if it happen to be in contact with large masses of these substances reacting upon one another. Fires are very frequently occasioned by the access of water to ships or warehouses in which quick-lime is stored.

421. When lumps of quick-lime are exposed to the air they slowly absorb both water and carbonic acid, and after a while fall to powder. This powder is known as **air-slaked lime.** When hydrate of calcium is stirred into water, there is formed not only a true solution, **lime-water,** which may be obtained clear and colorless by filtration, but also a turbid liquor consisting of particles of solid hydrate of calcium diffused through the lime-water; this liquor is known as **milk** or **cream of lime,** according to its consistency.

Both milk of lime and dry calcium hydrate absorb readily carbonic acid and hydrogen sulphide. For this purpose they are used in the purification of coal-gas. On this property of absorbing carbonic acid depends also in great measure the use of lime in mortar.

Mortar is commonly prepared by mixing 1 part of quick-lime with water enough to form a thin paste, then adding 3 or 4 parts of coarse, sharp sand, and thoroughly incorporating these ingredients. The paste thus obtained is applied as a thin layer to the moistened surfaces of the bricks or stones to be united. The pasty mortar soon sets to the hard mass above described, and, on continued exposure to the air, it slowly absorbs carbonic acid at its surface, and is there converted into a compact compound of hydrate and carbonate of calcium. The stone-like mass thus obtained binds firmly together the bricks or stones between which it has been interposed. The plastering used for finishing the walls and ceilings of rooms is mortar, to which a quantity of hair has been added to increase its tenacity ; in drying, it is, of course, subject to the same chemical changes as ordinary mortar.

422. **Calcium hydrate,** like sodium or potassium hydrate, exhibits a strong alkaline reaction when tested with moistened litmus-paper, and exerts a corrosive action upon most organic substances ; hence it is often called **caustic lime.** The value of lime, as an ingredient of composts to be used as manure, appears to depend, in great measure, upon its power of hastening the decay and disintegration of organic matter.

Exp. 196. — Add a few drops of water to a small quantity of dry calcium hydrate, and rub it to a paste between the fingers. It will be felt that the alkali acts upon the skin ; a little of the cuticle is really dissolved.

Lime is important, also, from being not only the cheapest alkali, but the cheapest of all the bases. It is used in the manufacture of the caustic alkalies, soda and potash ; of ammonia-water and of bleaching-powders ; as a flux in many metallurgical operations ; in the refining of sugar ; for preparing a lime-soap in the manufacture of "stearine" candles, and for numberless other purposes.

423. **Calcium sulphate** ($CaSO_4$) occurs in nature as the mineral **anhydrite.** The mineral **gypsum** is a hydrated calcium sulphate ($CaSO_4 + 2\,H_2O$). The same hydrated salt may be obtained by adding sulphuric acid, or the solution of some sulphate, to a strong aqueous solution of almost any of the salts of calcium.

When gypsum is heated moderately it is converted into the anhydrous calcium sulphate, which is often called **plaster of Paris.** If the anhydrous salt thus prepared be made into a paste with water, and then left to itself, it soon sets or hardens into a compact, coherent mass. This solidification is a consequence of the reassumption by the calcium sulphate of the two molecules of water of crystallization which were driven off by heat when the substance was made anhydrous.

On account of this property, plaster of Paris is largely used for making casts of various objects. It is also used in the manufacture of stucco and of various imitations of marble.

424. Ordinary **hydrated calcium sulphate** is soluble in about 400 parts of water at the ordinary temperature. It occurs in sea-water and also in most well- and spring-waters. Water containing calcium salts, such as the carbonate and sulphate, is "hard," and is not well adapted either for washing or for cooking.

Exp. 197. — Dissolve a small bit of the hard soap of Exp. 111 in hot water, and add to the solution an equal bulk of a solution of calcium sulphate. The mixture immediately becomes turbid, and after a few moments there will be formed a greasy, flocculent, adhesive scum upon the surface of the liquor. This precipitate is *lime-soap.*

Hard soap may be regarded as essentially sodium stearate; on the addition of calcium sulphate the metals calcium and sodium change places, sodium sulphate and calcium stearate being formed: the latter, as has been seen, is insoluble in water. When soap is added to hard water, it will neither produce any permanent froth nor cleansing effect, until the sulphate, or other lime-salt present, has all been decomposed; with such waters, much soap is consumed in removing the calcium compound, before the proper detergent action of the soap can be brought into play.

425. **Calcium Phosphate.** — The most important of the various calcium phosphates is the calcium phosphate ($Ca_3P_2O_8$) commonly called bone-phosphate, because found in bones. It is the chief of the inorganic constituents of which the skeletons of animals are composed. Small portions of it are found in most rocks and soils (§ **142**), it being a very widely diffused, though nowhere a very abundant substance. Considerable masses of it have been found, however, in Spain, New Jersey, North Carolina and Canada, and it is the principal ingredient of some kinds of guano. No matter whence obtained, it is a valuable manure when reduced to a fine powder. Though as good as insoluble in water, it dissolves readily in acids and in solutions of various organic substances.

When this calcium phosphate is treated with strong sulphuric acid there is formed a soluble hydrogen calcium phosphate ($H_4CaP_2O_8$), commonly called "**superphosphate of lime.**"

$$Ca_3P_2O_8 + 2\,H_2SO_4 = H_4CaP_2O_8 + 2\,CaSO_4.$$

Artificial *fertilizers* are made by thus treating ground bones with sulphuric acid. The reaction just given is also one step in the manufacture of phosphorus from bones.

In the manufacture of phosphorus the burnt bones are first treated with sulphuric acid. The soluble hydrogen calcium phosphate ($H_4CaP_2O_8$) is filtered from the insoluble calcium sulphate, mixed with charcoal, dried and ignited. The following reaction takes place; a portion of the phosphorus is set free and condensed under cold water, while the residue consists of a certain amount of calcium phosphate identical in composition with that originally contained in the bone ash: —

$$3\,H_4CaP_2O_8 + 10\,C = Ca_3P_2O_8 + 4\,P + 10\,CO + 6\,H_2O.$$

426. **Calcium chloride** ($CaCl_2$) may be prepared by dissolving chalk or marble in chlorhydric acid (as in **Exp. 75**), and evaporating the solution to dryness. When dried at about 200°, calcium chloride is left as a porous mass, which is largely employed in chemical laboratories for drying gases (Appendix, § 16). It absorbs water with great avidity, and is one of the most deliquescent substances known. When exposed to

air at the ordinary temperature, it soon absorbs so much water that it dissolves completely. At a low red-heat the anhydrous chloride melts to a clear liquid.

427. **Calcium hypochlorite** ($CaCl_2O_2$), as has been shown in **§ 85,** is a component of the substance commonly called "*chloride of lime.*" This important bleaching agent is prepared by passing chlorine gas into chambers filled with layers of finely-powdered slaked-lime. Chloride of lime, or bleaching-powder, is a dry, white powder, smelling feebly of hypochlorous acid; when exposed to the air, it slowly absorbs carbonic acid, and, at the same time, evolves chlorine: hence its employment as a disinfecting agent. If, instead of being left to be slowly acted upon by the carbonic acid of the air, it be treated with a dilute acid, — such as vinegar, — a copious evolution of chlorine will immediately occur. When heated, bleaching-powder gives off oxygen, and calcium chloride is left as a residue.

Exp. 198. — Fill an ignition tube one-third full of bleaching powder, and arrange the apparatus so that the gas may be collected over water. Heat the tube, and observe that the gas is expelled at a comparatively low temperature. 1 grm. of bleaching powder yields 40 or 50 c. c. of oxygen gas.

STRONTIUM (Sr) AND BARIUM (Ba).

428. The metals **strontium** and **barium** closely resemble calcium in appearance and properties. The specific gravity of strontium is 2.6; that of barium is 4.0. The atomic weight of strontium is 87.5, and that of barium 137. Like calcium, strontium and barium are both bivalent elements.

Most of the compounds of strontium and barium are closely analogous to the corresponding compounds of calcium. The oxides, peroxides, hydrates, carbonates, sulphates, nitrates, phosphates, chlorides, sulphides, etc., resemble in the main the corresponding calcium salts. The hydrates of strontium and barium are, however, more readily soluble in water than calcium hydrate, while their sulphates, nitrates and chlorides are less soluble than those of calcium. Barium sulphate is almost absolutely insoluble in water, and strontium sulphate is only very slightly soluble. Barium sulphate is found native, sometimes in considerable masses, as a very heavy white mineral called *barytes*,

which, when powdered, is largely employed for adulterating white lead. The name **barium** comes from a Greek word meaning *heavy*. Strontium salts are commonly prepared from the native carbonate, a mineral called **strontianite**, while the various salts of barium are obtained either from the native carbonate (**witherite**), or more commonly from the sulphate.

The colors imparted to the gas flames by the compounds of calcium, strontium and barium may be illustrated as follows : —

Exp. 199. — By means of iron wire, suspend three small bullets of well-burned coke from a ring of the iron stand. Heat the fragments in turn with the flame of the gas lamp, and observe the slightly yellowish flame which will be produced in each case ; then moisten one of the pieces of coke with a solution of calcium chloride, the second with a solution of barium chloride, and the third with a solution of strontium nitrate, and again heat them in turn with the gas flame. The calcium salt will impart a reddish-yellow color to the flame, the barium salt a green color, and the strontium salt a beautiful crimson.

LEAD (Pb).

429. The chief ore of lead is the native lead sulphide, **PbS**, the mineral galena, which is tolerably abundant in many localities, and is often associated with barium sulphate, fluor-spar, quartz and other common minerals ; it almost always contains a small proportion of silver sulphide. The carbonate of lead is also important as an ore in the United States.

Lead is a remarkably soft metal, of bluish-white color ; it can be readily cut with a knife, and may even be indented with the finger-nail ; it soils paper upon which it is rubbed. Its specific gravity is 11.4, and its atomic weight 207. It may be drawn into wire, and beaten into sheets, though, as contrasted with most of the other metals, it has but little tenacity. It melts at about 325°, and may be obtained in crystals by slowly cooling the molten metal.

The ready crystallization of lead furnishes a very simple method of separating this metal from the silver with which crude lead is almost always contaminated as it comes from the smelting furnaces. When melted argentiferous lead is allowed to cool slowly, and is at the same time briskly stirred, a quantity of solid crystalline grains separate

out after a while, and sink beneath the liquid metal, whence they may be dipped out in colanders. These crystals are composed of lead nearly free from silver, while all but a trace of the silver contained in the original lead is left in that portion of the metal which has not yet solidified; in a word, the alloy of lead and silver melts at a lower temperature than pure lead. The lead crystals on the one hand, and the silver alloy on the other, are methodically remelted and recrystallized until practically all the silver is concentrated in a rich alloy, from which the more precious metal is obtained by heating in a stream of air until all the lead is oxidized (process of cupellation).

430. When in thick masses, such as the common sheets and pipes of commerce, lead is scarcely at all acted upon by cold sulphuric acid, and is but slowly corroded by chlorhydric acid. Both these acids form, by their action on the lead, difficultly soluble salts; and as soon as a layer of the salt has once been deposited upon the surface of the metal, the latter is thereby protected from further corrosion. On exposure to the air, lead soon tarnishes, owing to the formation of a thin coating of a **lead suboxide.** By the simultaneous or alternate action of water and air, lead is very rapidly corroded in consequence of the formation of a **lead hydrate,** which is converted by the carbonic acid of the air into a **carbonate.** All natural waters act more or less on lead. In some cases the action is so slight that lead pipes are used with safety for conveying the water; in other cases the use of lead pipes is very dangerous on account of the poisonous character of the salts of lead.

431. **Lead protoxide** (**PbO**), commonly called **litharge,** may be obtained as a lemon-yellow powder by gently igniting the nitrate or carbonate. In the arts, litharge is prepared upon the large scale by heating metallic lead in a current of air; the color and texture of the product vary considerably according to the temperature and other conditions under which the litharge has been prepared.

Exp. 200.—Heat a small fragment of lead upon charcoal in the oxidizing flame of the blowpipe, and observe the gray film of suboxide which forms at first, and the yellow incrustation of litharge

which is obtained subsequently. The litharge may be melted if a strong, hot flame be thrown upon it.

Other oxides of lead are the **peroxide** (PbO_2), a dark brown powder formed by oxidizing litharge, and **red lead** or **minium**, which is a compound of PbO and PbO_2 in varying proportions.

432. **Lead sulphide** (PbS) occurs native as the mineral **galena.** It is also formed when hydrogen sulphide is passed into a solution of a lead salt. The precipitate which forms in this case is black or brown, or even red, if the solution be dilute. On account of the deep color, as well as the insolubility of this precipitate, hydrogen sulphide is often made use of as a means of detecting lead; the test is, in fact, so delicate that solutions containing only a hundred thousandth of their weight of metallic lead will assume a brown color on being charged with hydrogen sulphide.

433. **Other Salts of Lead.** — **Lead acetate**, a soluble, readily crystallizable salt, is much used in the arts. It has a sweet, astringent taste, whence the name **sugar of lead.** Like other lead salts, it is highly poisonous. **Lead carbonate** ($PbCO_3$), or rather compounds of the carbonate and hydrate in varying proportions, are used to an enormous extent as a white paint, under the general name of **white lead.** The native lead carbonate is an important ore of the metal. **Lead silicate** is of interest from being an important ingredient of flint glass; a certain proportion of it renders glass lustrous and very beautiful. Such glass is, however, soft and easily fusible. It is, moreover, rather easily acted upon by alkalies, acids and other chemical agents, and is hence not well suited for use in the chemical laboratory.

434. In many points of chemical behavior the compounds of lead resemble more or less clearly the corresponding compounds of barium, strontium and calcium. It is, moreover, bivalent, like the elements in question. Lead is, therefore, classed as a member of the **calcium group**, although, as in the case with fluorine in the chlorine group, it differs in some respects from the other members of the family.

CHAPTER XXV.

MAGNESIUM, ZINC, AND CADMIUM.

MAGNESIUM (Mg).

435. The compounds of **magnesium** are found widely diffused, and rather abundantly, in nature. The bitter taste of sea-water and of some mineral waters is due to the presence of magnesium salts, while magnesium silicate and carbonate are contained in a variety of minerals, and in such common rocks as dolomite, serpentine, soapstone and talc.

436. **Metallic magnesium** may be prepared by heating anhydrous magnesium chloride with metallic sodium, and subsequently dissolving out in cold water the sodium chloride which results from the reaction. **Magnesium** is a lustrous metal, as white as tin ; its symbol is **Mg** and its atomic weight 24. It does not tarnish in dry air, though in damp air it soon becomes covered with a film of magnesium hydrate. Cold water acts on magnesium only slowly ; hot water acts more rapidly, magnesium oxide being formed and hydrogen being set free. The metal dissolves readily in almost any acid with evolution of hydrogen. It melts at a low red heat, and volatilizes at higher temperatures ; it may be readily distilled at a bright red heat. When heated strongly in the air it takes fire and burns with a bluish-white light of great brilliancy and high **actinic power.** The metal is employed by photographers for illuminating caverns and other places into which sunlight cannot penetrate, and in cloudy weather it is even used by them as a substitute for daylight. The metal can be pressed into wire or into thin ribbons, and a considerable quantity of it is now used in both these forms for purposes of illumination.

437. **Magnesium Oxide** or **Magnesia** (**MgO**). — There is but one compound of magnesium and oxygen ; it is obtained as a white amorphous powder when magnesium is burnt in the air,

or it may be prepared by igniting the carbonate, chloride or nitrate.

Exp. 201. — Roll 10 or 12 c. m. of magnesium wire or thin ribbon into a coil around a small pencil ; withdraw the pencil and place in its stead a piece of iron wire or a knitting-needle ; holding this wire horizontally, apply a lighted match to the end of the magnesium coil ; the magnesium will burn to the white oxide which coheres in an imperfect coil, clinging to the iron wire. A portion of the oxide goes off as white smoke.

The oxide is tasteless and odorless. It is altogether infusible at temperatures short of that of the oxy-hydrogen flame. Very excellent crucibles for scientific purposes are prepared by compressing magnesium oxide into suitable forms.

438. **Salts of Magnesium. — Magnesium chloride** ($MgCl_2$) is found in sea-water and many saline springs. **Magnesium sulphate** ($MgSO_4$), or rather the hydrated compound ($MgSO_4 + 7\ H_2O$), is known as **Epsom salts** on account of its occurrence in a mineral spring at Epsom, England. It occurs in other springs, and is made artificially from various native minerals containing magnesium. It is a colorless crystalline salt, readily soluble in water, and having a bitter taste. It is much used in medicine. **Magnesium carbonate** ($MgCO_3$) occurs native as the mineral **magnesite**. The *magnesia alba* of the shops is a varying mixture of magnesium carbonate and hydrate, and is prepared by adding sodium carbonate to a hot solution of magnesium sulphate.

ZINC (Zn).

439. **Zinc** does not occur in nature in the metallic state, but in combination with other elements such as oxygen (**red oxide of zinc**) and sulphur (**zinc sulphide,** or **blende**) ; the carbonate and the silicate of zinc are also native minerals.

Zinc is a bluish-white metal of crystalline texture, brittle at the ordinary temperature, and also when heated above 200°, but at a temperature of about 130° or 140° it may easily be rolled out or hammered into sheets. The metal melts at 425°, and

boils at a bright red heat : in presence of air the red-hot metal takes fire and burns with a brilliant bluish-white light and formation of a dense cloud of white oxide of zinc.

If a strip of thin sheet zinc be held in the flame of the gas lamp, it can readily be burned to oxide. The experiment succeeds best with zinc leaf, which instantly burns with a vivid flame and formation of floating flocks of the white oxide. In oxygen gas, zinc burns with peculiar brilliancy.

Exp. 202. — Mix intimately in a mortar 20 grms. of dry granulated zinc (or zinc dust, if it can be obtained) and 40 grms. of crude saltpetre ; heat to redness a small Hessian crucible in an anthracite fire ; remove the crucible from the fire, and place it in such position that any fumes which may subsequently be evolved from it shall be drawn into the chimney. By means of a spoon or ladle, project into the red-hot crucible the mixture of zinc and saltpetre, taking care to stand away as far as possible from the crucible. The greater part of the metal will burn fiercely, at the expense of the oxygen in the saltpetre, though a portion of it will be volatilized by the intense heat of combustion and converted into zinc oxide in the air. The residue in the crucible is a soluble compound known as potassium zincate.

Granulated zinc is much used in chemical laboratories, for a variety of purposes, but particularly for preparing hydrogen (§ 35). It may be prepared by melting the zinc in a Hessian crucible and heating the melted metal nearly to redness. The crucible is then removed from the fire and its contents poured, in a thin stream, from a height of 6 or 8 feet into a vessel of cold water. This process of *granulation* or *feathering* may be conveniently applied to any of the other easily fusible metals, such as bismuth, lead or tin, when they are required in a finely divided condition.

In the manufacture of zinc a quantity of the vaporized metal is condensed in a very fine state of division corresponding to the "flowers of sulphur." This zinc dust (which contains also, some zinc oxide) is already used to a considerable extent in Europe in indigo-dyeing in the manner illustrated by Exp. 159, but has not yet become an ordinary article of commerce in this country. It is a very convenient form of the metal for many experimental purposes.

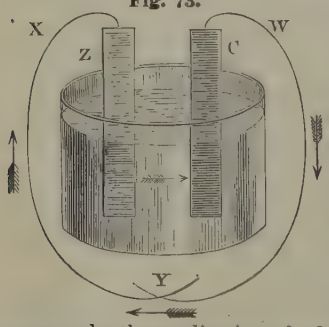
440. **Zinc** is not much acted upon either by moist or dry air, at the ordinary temperature, as it soon tarnishes and becomes covered with a thin film of a basic carbonate of zinc, which

adheres closely to the metal, and protects it from further change. Owing to this durability, the metal is much used in the form of sheets. Sheet iron and iron wire also are often covered with a protecting coating of zinc, and are then said — most improperly — to be **galvanized.** Zinc forms several valuable **alloys;** brass is an alloy of zinc and copper, and German silver is a brass whitened by the admixture of a small proportion of nickel. The specific gravity of zinc varies from 6.8 to 7.3; its atomic weight is 65.

441. **Zinc** is readily attacked and dissolved by acids, in most instances with evolution of hydrogen. The chemical action of dilute acids upon zinc is a very common source of that peculiar mode of force called a **galvanic current.** There are few, if any, chemical reactions which cannot be made to produce electricity, and in general, the more powerful the chemical action, the more powerful is the electrical action which results.

Exp. 203. — Solder a piece of stout copper wire to one end of a strip of sheet zinc, 4 c. m. wide by 10 c. m. long. The soldering will be readily effected by rubbing the zinc and the wire in the vicinity of the proposed place of contact, with a strong solution of zinc chloride, before applying the melted solder. In the same way, solder a similar wire to a like strip of bright sheet copper. Place the strips of zinc and copper in a vessel filled with water, acidulated with 1-12 to 1-10th its volume of sulphuric acid in such a way that the two strips shall not touch each other either within or without the liquid. As long as the wires coming from the strips of metal do not touch each other, the copper remains quiescent, while the zinc is attacked, and bubbles of gas rise from its surface; but if the two copper wires are brought into close contact, by means of a binding-screw, or by the application of solder, the following phenomena occur: 1st. Minute bubbles of hydrogen gas will be evolved from the surface

Fig. 73.



of the copper plate. 2d. The zinc dissolves more rapidly than before, and at the close of the experiment, zinc sulphate may be recovered from the liquid in the beaker. 3d. This transfer of the hydrogen from the zinc to the copper instantly ceases, if the contact between the wires is destroyed. 4th. If the two wires be connected with the two ends of the coil of wire which surrounds the magnetic needle of the common galvanometer, the deflection of the suspended needle will demonstrate the fact that an electric current is passing through the wires from one plate of metal to the other.

This experiment well illustrates the principle on which a large class of batteries employed in telegraphing and in electro-metallurgy are constructed and worked, except that the corrosion of the zinc is generally hindered by coating it with mercury.

442. When zinc is immersed in the solution of a lead salt, such as the nitrate or acetate, zinc dissolves, and lead is deposited in the metallic state : $PbN_2O_6 + Zn = ZnN_2O_6 + Pb$.

Exp. 204.—Dissolve 10 grms. of lead acetate in 250 c. c. of water, add a few drops of acetic acid in order to dissolve the cloudy precipitate of lead carbonate, which is formed from the carbonic acid in the water, pour the solution into a wide-mouthed bottle and suspend in it a strip of sheet zinc. The zinc will soon be covered with a brilliant coating of crystalline spangles of metallic lead, and this *crystalline vegetation*, which is known as the *lead-tree*, will continue to grow until all the lead has been deposited from the solution ; the latter will now contain nothing but zinc acetate.

Fig. 74.

If, in this experiment, the piece of zinc be weighed before and after its immersion in the lead acetate, and if the precipitated lead be also weighed, it will be found that the weight of the lead obtained is to the weight of the zinc dissolved very nearly as 207 is to 65,— that is, as the atomic weights of lead and zinc respectively. This experiment is interesting as illustrating the general law of the replacement of one metal by another according to a fixed proportion ; when the quantivalence (see § 74) of the two metals is the same, this proportion is the ratio of the atomic weights ; when the quantivalence is different, the proportion is some multiple of this ratio. Thus, in the foregoing experiment, for every atom of lead precipitated an atom of zinc was dissolved. In the similar case represented by the following equation one atom of zinc takes the place of two atoms of silver : —

$$2\,AgNO_3 + Zn = ZnN_2O_6 + 2\,Ag.$$

443. **Electro-chemical Relations of the Elements.** — Other substances, besides the zinc and copper of Exp. 203, if brought into contact in a liquid capable of affecting them unequally, exhibit similar electrical phenomena. It is necessary that the substances should both be conductors of electricity, and that the liquid should contain some compound capable of such decomposition that there shall be formed a new compound containing one of the substances immersed in the liquid. When the two substances, as in Exp. 203, are connected by means of a copper wire, a current of electricity passes along the wire in each direction; the current which passes from the zinc to the copper in the liquid, and from the copper to the zinc in the air, is called the *positive current*, and under such conditions the zinc is said to be *positive* with reference to the copper.

When the wire which connects the two plates is cut, the flow of electricity ceases; but if the two extremities of the wires be immersed in some conducting liquid, the flow is re-established. In many cases the passage of the current through a liquid affects its decomposition. The two extremities of the wires are called *poles;* that connected with the negative plate is called the positive pole, and that connected with the positive plate is called the negative pole. If the poles of a galvanic battery be immersed in a solution of zinc chloride ($ZnCl_2$), for example, this salt is decomposed by the action of the electrical current; the atoms of zinc go to the negative pole, and hence are called *positive*, with reference to the atoms of chlorine, which are called *negative*, because they go to the positive pole. With reference to other metals, as to magnesium, for instance, zinc is negative. The terms positive and negative are thus seen to be merely relative, and under certain circumstances the relation of one element to another may be directly reversed.

Negative End —.
OXYGEN.
SULPHUR.
NITROGEN.
FLUORINE.
CHLORINE.
BROMINE.
IODINE.
PHOSPHORUS.
ARSENIC.
BORON.
CARBON.
ANTIMONY.
SILICON.
HYDROGEN.
GOLD.
PLATINUM.
SILVER.
MERCURY.
COPPER.
TIN.
LEAD.
COBALT.
NICKEL.
IRON.
ZINC.
MANGANESE.
ALUMINUM.
MAGNESIUM.
CALCIUM.
SODIUM.
POTASSIUM.
Positive End +.

It is possible to arrange the chemical elements according to their electro-chemical characters, as ordinarily exhibited, so that each ele-

ment in the series will be positive to any element placed above it, and negative to any one given below it. On page 256 the elements are so arranged. Speaking somewhat loosely, all the elements which in this list precede *gold* are negative, while gold and the elements which follow it are positive. The negative elements are spoken of collectively as the non-metallic elements, while the positive are known as the metallic elements.*

The property which one metal possesses of replacing another in its salts, as illustrated by Exp. 204, is an exhibition of this same relation. Metallic copper may be thrown down from a solution of one of its salts by the introduction of metallic iron or zinc; a little metallic mercury put into a solution of silver nitrate will cause the formation of a *silver-tree*. In these cases the metal which goes into solution is said to be electro-positive to the metal which is precipitated, and the latter is electro-negative to the former.

444. **Salts of Zinc.** — **Zinc oxide** (**ZnO**) is formed when metallic zinc is burned in the air, and may also be prepared by igniting the carbonate. Under the name of **zinc white,** it is somewhat largely employed as a white paint. It dissolves readily in acids. **Zinc chloride** (**$ZnCl_2$**) is a white, soluble, deliquescent substance, formed by dissolving zinc in chlorhydric acid. It is used for preserving timber, also in soldering to cleanse the surface of the metal. **Zinc sulphate** (**$ZnSO_4$**), or rather the hydrated compound (**$ZnSO_4 + 7\ H_2O$**), known as *white vitriol*, is used to a certain extent in medicine, and also in the arts.

CADMIUM (Cd).

445. **Cadmium** is a comparatively rare metal, found associated with zinc in nature; it is remarkably similar to zinc in its chemical relations. It is a bluish-white lustrous metal, tarnishing somewhat when exposed to the air. It melts and volatilizes at temperatures below redness. Heated in the air, it takes fire and burns to a brown oxide. **Cadmium sulphide** is of a bright yellow color, and has been used as a pigment.

* See in this connection some additional statements on page 293.

CHAPTER XXVI.

ALUMINUM, GLUCINUM, CHROMIUM, MANGANESE, IRON, COBALT AND NICKEL.

ALUMINUM (Al.)

446. **Aluminum** is perhaps the most abundant element upon the earth's surface, next to oxygen and silicon. It is the most abundant of all the metals, as much as a twelfth of the solid crust of the globe being composed of it. It occurs in enormous quantities in combination with oxygen and silicon, in most rocks and soils. It is contained in clay, marl and slate, as well as in feldspar, mica and many other common minerals.

Although the compounds of **aluminum** are so abundant, no cheap method of obtaining the metal itself has yet been devised. For this reason it cannot be applied to many uses for which it is otherwise well suited. It is generally prepared by heating metallic sodium either with chloride or fluoride of aluminum, or with a double chloride or fluoride of aluminum and sodium.

447. **Aluminum** is a bluish-white metal, of remarkable lightness. Its specific gravity, 2.56, is about the same as that of porcelain, and only about a quarter of that of silver. The metal is malleable, ductile and tenacious, and may be beaten into thin sheets, like gold and silver, and drawn into fine wire. It is remarkably sonorous : a bar of it suspended by a wire rings with a clear musical note on being struck. Aluminum-bronze, an alloy of 90 parts copper and 10 parts aluminum, is exceedingly hard, very malleable, as tenacious as steel, of a beautiful golden color, and susceptible of being highly polished.

448. **Aluminum oxide,** or **alumina** (Al_2O_3), occurs native, as the minerals corundum, ruby and sapphire. Emery is impure aluminum oxide.

Aluminum hydrate ($Al_2H_6O_6$) may be obtained as a gelatinous, flocculent precipitate, by adding ammonia-water to the solution of an aluminum salt. The hydrate dissolves readily in acids forming aluminum salts; it also dissolves in caustic alkalies forming a class of salts called **aluminates.**

Exp. 205. — Heat a small fragment of aluminum sulphate (common alum will answer equally well) with water in a test-tube until it has completely dissolved, pour half the solution into another tube, and add to it, drop by drop, ammonia-water, until the odor of ammonia persists after the mixture has been thoroughly shaken. Aluminum hydrate will be precipitated in accordance with the reaction: —

$$Al_2\,3\,(SO_4) + 6\,(NH_4)HO = Al_2H_6O_6 + 3\,(NH_4)_2SO_4.$$

Put two or three drops of the moist aluminum hydrate into another test-tube and cover them with ammonia-water; no clear solution will be obtained, for aluminum hydrate is but slightly soluble in ammonia-water.

Put two or three drops of the moist aluminum hydrate into still another test-tube, and cover them with a solution of sodium hydrate; the precipitate will dissolve immediately; sodium aluminate is formed, and this salt is easily soluble.

Exp. 206. — Take another portion of the clear solution of aluminum sulphate prepared in Exp. 205, and add to it, drop by drop, a dilute solution of caustic soda. A precipitate will soon fall, as in Exp. 205, and if no excess of sodium hydrate were added, this precipitate would remain undissolved, but on adding more of the soda solution the precipitate dissolves at once, with formation of sodium aluminate ($Na_2Al_2O_4$).

449. **Aluminum hydrate** combines readily with many organic coloring-matters, forming compounds insoluble in water.

Exp. 207.—Take a small quantity of the solution of cochineal prepared in Exp. 154, add to it an equal bulk of a solution of aluminum sulphate (or of common alum), and then add to the mixture ammonia-water, as in Exp. 205. A colored precipitate, consisting of aluminum hydrate and of the coloring matter of the cochineal, will be thrown down; it is the substance called carmine-lake. Similar precipitates may be prepared by substituting almost any other organic coloring matter for the cochineal of this experiment. Precipitates thus formed by the union of a metallic hydrate and a coloring matter are classed as *lakes.*

450. **Mordants.** — The fibre of cotton, when impregnated with alumina, can be made to retain colors which the cotton itself has no power to hold, **Exp. 156, § 339**: hence the use of aluminum salts as **mordants** in dyeing. In fact, mere immersion in a solution of a salt of aluminum suffices to make a great difference in the amount of coloring matter taken up by cotton. An acetate of aluminum is much employed in dyeing, because when exposed to the air on the cloth it is partly decomposed, a certain amount of acetic acid is set free and volatilized, leaving the fibres impregnated with aluminum hydrate or oxide.

Exp. 208. — Prepare an acetate of aluminum as follows: — Dissolve 6 grms. of sugar of lead (lead acetate) in 8 c. c. of hot water; also dissolve 8 grms. of common alum in 12 c. c. of hot water; mix the two solutions and filter off the insoluble lead sulphate which is formed. In the solution thus prepared, soak a piece of cotton cloth, and then hang it up in a moist and warm atmosphere for several days. Treat this cloth, as well as a piece of ordinary cotton of the same size, with a solution of logwood as described in Exps. 156, 157, and observe the difference in the amount of color imparted to the fabric.

Other oxides or hydrates besides the aluminum hydrate are used as mordants. An acetate of iron made by dissolving scraps of iron in the crude pyroligneous acid obtained by the destructive distillation of wood (§ 238) is much used by dyers; salts of tin, of chromium and of other elements are employed to a greater or less extent.

451. **Aluminum sulphate** ($Al_2\,3\,(SO_4)$) is prepared by treating hot roasted clay, which is an aluminum silicate, with sulphuric acid. The mixture of aluminum sulphate and silica obtained is called **alum-cake,** and from it the aluminum sulphate can be obtained by treating with water, which dissolves the aluminum sulphate and leaves the silica behind. Aluminum sulphate is employed as the source of the various compounds of aluminum used in dyeing and calico-printing.

452. **Alums.** — **Potassium alum** is an aluminum potassium sulphate crystallizing in sharply defined crystals. Its composition is represented by the formula $Al_2K_2\,4\,(SO_4) + 24\,H_2O$. It is known as *common alum*, although of late years **ammonium**

alum has to a considerable extent taken its place. The formula of ammonium alum is $Al_2(NH_4)_2 4(SO_4) + 24 H_2O$.

453. **Aluminum Silicates.** — Of all the aluminum compounds the silicates are by far the most important. Clay in all its varieties is a hydrated aluminum silicate, usually mixed with an excess of silica, besides other impurities derived from the rocks from whose decomposition the clay itself has been formed. Clay is remarkable on account of its plasticity when moist, of the facility with which it is converted into stone-like masses when strongly heated, and of its infusibility when pure.

Earthenware, bricks, and ordinary pottery are made from common clay, by mixing the clay with water enough to form a plastic paste, which is then moulded into any desired form, dried and intensely ignited. The red color of certain varieties of ware is due to the iron oxide they contain. Porcelain is made from a very pure clay (kaolin). The glaze on articles of pottery is made by coating them with an easily fusible substance, such as a mixture of litharge and clay, or in the case of porcelain finely ground feldspar, and subjecting them thus coated to high heat. Ordinary stone-ware is glazed by throwing common salt into the kiln. The salt volatilizes and coming in contact with the heated ware it is decomposed, and a fusible silicate results which renders the articles impervious to moisture.

GLUCINUM (Gl) and INDIUM (In).

454. **Glucinum** is a rather rare metal, found, together with aluminum, in the emerald, in beryl and in a few other minerals. It closely resembles aluminum in its chemical and physical properties. The atomic weight of glucinum is 14; its symbol is **Gl.**

455. **Indium** is a rare metal, found associated with zinc in certain ores, and was discovered by means of spectrum analysis. It is a soft white metal. Its atomic weight is 113.4; its symbol **In.**

CHROMIUM (Cr).

456. The chief ore of **chromium** is a compound of iron, chromium, and oxygen ($FeCr_2O_4$) called **chrome iron-ore.** The compounds of chromium are somewhat extensively employed in the arts.

457. **Chromium sesquioxide** (Cr_2O_3) prepared by igniting the hydrate ($Cr_2H_6O_6$), is a green powder somewhat used as a pigment. The hydrate may be obtained by adding ammonia-water to a solution of a salt of chromium. It forms a bulky green precipitate.

458. **Chromium sulphate** ($Cr_2\,3\,(SO_4)$) is sometimes prepared in the pure state; generally, however, it is prepared in combination with potassium (or ammonium) sulphate forming **chrome alum,** a beautiful violet crystalline salt. The formula of ordinary chrome alum is $Cr_2K_2\,4\,(SO_4) + 24\,H_2O$.

Exp. 209. — Dissolve 15 grms. of powdered potassium bichromate in 100 c. c. of warm water; cool the solution, and then add to it 25 grms. of concentrated sulphuric acid; cool the liquor again, and pour it into a porcelain dish, surrounded with cold water; slowly stir into the mixture 6 grms. of alcohol, and set the whole aside. In the course of 24 hours, the bottom of the dish will become covered with well-defined, octahedral crystals of chrome alum.

In this experiment the chromic acid which is set free by the sulphuric acid gives up a part of its oxygen to the alcohol, and is converted into chromium sulphate, which unites with the potassium sulphate to form chrome alum: the alcohol is oxidized in part to aldehyde (§ 235) (the peculiar odor of which is distinctly perceived) and partly to acetic acid.

459. **Chromic anhydride** (CrO_3) may be obtained by treating potassium bichromate with sulphuric acid. The chromic anhydride separates in red crystals, which dissolve in water with formation of **chromic acid** (H_2CrO_4). Several of the **chromates** find application in the arts, as the normal potassium chromate (K_2CrO_4), the potassium bichromate ($K_2Cr_2O_7 = K_2CrO_4,CrO_3$) and the lead chromates.

MANGANESE (Mn).

460. **Manganese** is a grayish-white, hard, brittle metal, the principal ore of which is the binoxide (MnO_2), which has already been employed in the generation of oxygen (**Exp. 4, § 12**) and of chlorine (**Exp. 30, § 78**). The residue in the latter case consisted of **manganese chloride,** which may be

obtained in pink crystals ($MnCl_2 + 4\,H_2O$) by filtering the liquid left in the flask and evaporating the solution until it crystallizes.

There are several oxides of manganese besides the binoxide.

461. **Manganic anhydride** (MnO_3) and **manganic acid** (H_2MnO_4) have never been obtained in a free state. Several of the **manganates**, however, are well-known bodies. **Potassium manganate** (K_2MnO_4) may be made by fusing together manganese binoxide, caustic potash, and potassium chlorate. The manganate is soluble in water, the solution being of a green color. When this green solution is boiled **potassium permanganate** ($K_2Mn_2O_8$) is formed, which gives a dark purple colored solution. The manganates and permanganates readily give up oxygen and lose their color; even a piece of wood or paper thrown into the green or red solution of a manganate, or permanganate, will quickly abstract oxygen from the solution and destroy its color. Potassium permanganate is largely employed for disinfecting putrid water, as well as animal or vegetable matters in a condition of putrefaction. The oxidizing action of potassium permanganate may be shown by the following experiment.

Exp. 210. — In a beaker or flask dissolve 0.25 grm. of crystallized oxalic acid in 50 c. c. of water, add 5 c. c. strong sulphuric acid, and warm the solution to about 60°. Then add a solution of potassium permanganate *drop by drop*, and observe that the color is at first immediately destroyed. Continue to add the permanganate until it is no longer decolorized. The reaction that has taken place may be thus represented: —

$$K_2Mn_2O_8 + 5\,C_2H_2O_4 + 3\,H_2SO_4 =$$
$$2\,MnSO_4 + K_2SO_4 + 8\,H_2O + 10\,CO_2.$$

The oxalic acid ($C_2H_2O_4$) is entirely converted into water and carbonic acid: the potassium permanganate gives up its oxygen and is converted into a mixture of manganese and potassium sulphates.

On this property of potassium permanganate are based methods for the quantitative estimation of readily oxidizable substances such as oxalic acid or the ferrous salts.

IRON (Fe).

462. Although **iron** is one of the most widely diffused and most abundant of the metals, it is rarely found native in the metallic state. Meteors, however, fall upon the earth from outer space, which consist mainly of metallic iron, contaminated with several other elements in small proportions. Minerals containing iron occur in great numbers; and there are indeed few natural substances in which iron is not present. It is found in the ashes of most plants, and in the blood of animals. The natural compounds of iron which are available as ores of the metal are chiefly oxides and carbonates.

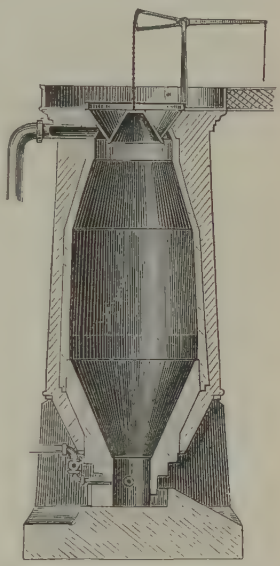
From the richer iron-ores a very excellent iron can be obtained by simply heating the broken ore with charcoal in an open forge fire, urged by a blast. The ore is deoxidized by the carbon of the fuel, and the reduced iron is agglomerated into a pasty lump called a "**bloom,**" while the earthy impurities contained in the ore combine with a portion of the oxide of iron to form a fusible glass or **slag.** This process is not economical in the chemical sense, for much iron is lost in the slag, and much fuel is burnt to waste in an open fire, but when well conducted it yields an admirable quality of iron, and is easily practised by people possessing but little mechanical skill and no chemical knowledge; it is undoubtedly the oldest method of extracting iron from its ores.

463. In the extraction of iron from its common ores, the metal is usually obtained, not pure, but in a carburetted fusible state, known as **cast-iron** or **pig-iron.** The main features of the process are, first, a previous **calcination** or **roasting** to expel water, carbonic acid, sulphur and other volatile ingredients of the ore; secondly, the **reduction** of the oxide of iron to the metallic state by ignition with carbon; thirdly, the separation of the earthy impurities of the ore by fusion with other matters into a crude glass or **slag;** and lastly, the **carbonizing** and melting of the reduced iron. The preliminary calcination is not always essential, but with many ores, especially the carbonates and hydrates, it is very desirable; not unfrequently all the

drying necessary is effected in the upper part of the blast-furnace itself, within which the three last steps of the process always take place.

The **blast-furnace** for iron consists essentially of a double cone, built of fire-brick and masonry, and is about 50 feet in height, and from 15 to 18 feet in width at its broadest part. An idea of its construction may be obtained from Fig. 75. The furnace is closed at the bottom, the air necessary for the support of the combustion being supplied by a powerful blast blown through pipes called *tuyères* (pronounced *tweers*). At the high temperature produced the carbon of the fuel removes the oxygen from the iron-ore, and the metallic iron is set free. The reduction of the oxide of iron, however, is not alone sufficient to secure the metal; iron-ores almost always contain earthy admixtures, consisting chiefly of silica, clay and calcium carbonate, and these substances are so intimately mixed with the reduced metal, that it is essential to melt them before the iron can separate by virtue of its greater specific gravity. This is brought about by converting these impurities into fusible double silicates by the addition of some proper substance which is called a *flux*. With ores in which the earthy admixture is chiefly calcareous, the flux must be clay or some siliceous material, but in the more frequent case of ores containing clay or silica the flux will be limestone or quicklime. In either case a fusible double silicate of aluminum and calcium is the essential constituent of the slag.

Fig. 75.



The blast furnace is charged at the top with alternate layers of the fuel, (which may either be charcoal, anthracite or coke) the ore and the flux, which is generally lime; and air is constantly supplied in immense quantities at the bottom of the furnace. The blast coming in contact with a great excess of incandescent carbon, there is formed immediately carbon protoxide, and this gas, together with

the unaltered nitrogen ascends the shaft. The layers of solid material thrown in at the top of the furnace gradually sink down, and as soon as a stratum of ore has descended sufficiently to be heated by the hot mixture of nitrogen and carbon protoxide it becomes reduced to spongy metallic iron, which, mixed with the flux and the earthy impurities of the ore, settles down to hotter parts of the furnace, where it enters into a fusible combination with carbon, while the flux and earthy impurities melt together to a liquid slag. The liquid carburetted iron settles to the very bottom of the furnace, whence it is drawn out, at intervals, through a *tapping-hole* which is stopped with sand when not in use. The viscous slag flows out over a dam, so placed as to retain the iron, but to allow the escape of the slag which floats on the iron, as fast as it accumulates in sufficient quantity. As fresh portions of the ore, fuel and flux are continually supplied, and the iron is withdrawn from time to time, the process goes on without interruption sometimes for several years.

The gases which issue from the mouth of the blast-furnace are charged with an enormous heating power, for besides being themselves intensely hot they contain, even after having effected the reduction, a large proportion of combustible gases, such as carbon protoxide, carburetted hydrogen and hydrogen. They are, therefore, collected at the top of the furnace by a sort of conical hood, conducted off through a pipe, and burned in suitable furnaces, the heat produced being utilized in raising the temperature of the blast of air forced into the furnace through the *tuyères*.

Cast-iron contains from 2 to 6 per cent of carbon ; in *white* iron, which is hard and brittle, and of crystalline texture, the carbon seems to be mainly in combination with the iron ; while in *gray* iron, which is slightly malleable and of granular texture, the carbon exists chiefly as graphite mechanically disseminated through the iron. Cast-iron also contains a small amount of silicon and not unfrequently manganese ; it is, moreover, usually contaminated with minute quantities of sulphur and phosphorus.

464. The production of malleable or **"wrought"-iron** from cast-iron consists essentially in burning out the carbon, silicon, sulphur and phosphorus which cast-iron contains. This oxidation of the impurities of cast-iron is effected by a process known as **puddling**. The operation consists in melting the iron in a **reverberatory furnace** and stirring it so that the air will come in contact with it.

Fig. 76 represents a reverberatory furnace, such as is used in puddling. The principle of this furnace has already been explained in § 370.

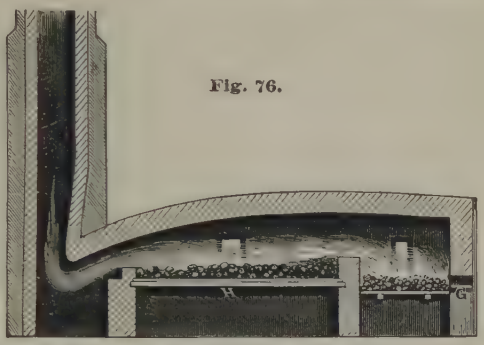


Fig. 76.

In puddling it is customary to add to the charge of pig-iron a quantity of iron scale or other oxide of iron. The oxidation of the silicon, carbon, phosphorus, and other impurities is effected partly by the air but chiefly by the oxide added to the charge. When the cast-iron is so far decarbonized as to be pasty in the fire, it is gathered into lumps on the end of an iron bar and carried from the furnace to a hammer or squeezer which expresses the liquid slag and welds into a coherent mass the tenacious iron. The wrought-iron thus produced has a gray color, is malleable and may be welded at a red heat. It still contains from 0.05 to 0.25 per cent of carbon.

465. **Steel.** — Intermediate in composition between cast- and wrought-iron as far as the amount of carbon is concerned is the invaluable substance, — **steel.** It may be made from wrought-iron by heating bars of iron to redness for a week or more in contact with powdered charcoal in close boxes from which air is carefully excluded. Though the iron is not fused, nor the carbon vaporized, yet the carbon gradually penetrates the iron and alters its original properties; when the bars are withdrawn from the chests in which they were packed, the metal has become fine-grained in fracture, more brittle and more fusible, and contains from 1 to 2 per cent of carbon. This process of preparing steel is called the **"cementation" process;** it is a curious instance of chemical action between solid materials which are apparently in a state of rest.

466. A new and very rapid method of preparing cast-steel

directly from cast-iron is that known as the **Bessemer process.** From two to six tons of cast-iron, previously melted in a suitable furnace, are poured into a large covered crucible, called the **converter,** which is made of the most refractory materials, and swung on pivots in such a manner that it can be tipped up and emptied by means of an hydraulic press. Through numerous apertures in the bottom of the crucible a blast of air is forced up into the molten metal; the combustion of the carbon and silicon of the iron, as well as of a portion of the iron itself, causes an intense heat, which keeps the mass fluid in spite of its rapid approach to the condition of malleable iron. Towards the end of the operation a sufficient quantity of *spiegeleisen* is introduced into the crucible. This *spiegeleisen* is a peculiar alloy of iron, manganese and carbon: the manganese removes some of the oxygen previously combined with iron and some sulphur; the carbon converts the whole mass into steel, and the melted steel is immediately cast into ingots.

The symbol of iron is **Fe** (Latin, *ferrum*); its atomic weight is 56.

467. **Oxides and Hydrates of Iron.** — The best known of the compounds of iron and oxygen are the **protoxide** (**FeO**), or **ferrous oxide,** as it is often called; the **sesquioxide** (**Fe_2O_3**), often called **ferric oxide;** and the **magnetic oxide** (**Fe_3O_4**).

468. **Iron protoxide** or **ferrous oxide** (**FeO**) may be obtained by igniting ferrous oxalate in close vessels; it absorbs oxygen so rapidly that it takes fire when brought in contact with the air. **Ferrous hydrate** (**FeH_2O_2**), obtained by adding caustic alkali to a solution of a ferrous salt, is a white precipitate which rapidly changes on exposure to the air by taking on oxygen.

469. **Iron sesquioxide** or **ferric oxide** (**Fe_2O_3**), called also **red oxide of iron,** occurs abundantly in nature as hematite, specular iron and red ochre. It is valuable as an ore of iron. It is also prepared artificially, and is much used as a pigment. A fine variety, known as *rouge*, is used for polishing glass and jewelry. By heating ferric oxide in a current of hydrogen, or other reducing gas, metallic iron is readily obtained. This oxide

of iron is called *sesquioxide* because it contains once and a half as many atoms of oxygen as of iron (*sesqui*, Latin, one and a half).

Ferric hydrate ($Fe_2H_6O_6$) may be prepared by adding an excess of ammonia-water to the solution of almost any ferric salt.

Exp. 211. — Cover a teaspoonful of fine iron filings or small tacks with 8 or 10 c. c. of dilute sulphuric acid in a small bottle ; when the evolution of hydrogen slackens, dilute with an equal bulk of water and filter into a small flask. To the liquid add a few drops of strong nitric acid, and heat it to boiling. The liquor will soon be colored dark-brown by the nitrous fumes resulting from the decomposition of the nitric acid, which are for a short time held dissolved by the liquid ; but this deep coloration soon passes away, and there is left only the yellowish-red color of the ferric sulphate which has been formed. Add to the solution ammonia-water, until the odor of the latter persists after agitation, and collect upon a filter the flocculent red precipitate of ferric hydrate.

470. There are several ferric hydrates which occur in nature and differ somewhat in composition from this the normal hydrate. **Yellow ochre** is a variety of ferric hydrate. The readiness with which ferric oxide gives up oxygen to reducing agents is shared by the hydrate as well. The iron nails employed in the construction of ships, bridges, fences, or shoes, actually corrode, "eat up" or "burn out" the organic matter in contact with them, by absorbing oxygen from the air and transferring it to the carbon compound with which they are in contact. The rotting of canvas by iron rust, or of a fishing-line by the rusty hook, are familiar instances of corruption by rust.

Ferric hydrate readily absorbs sulphuretted hydrogen with formation of an iron sulphide ; it is much used on this account in the purification of coal-gas.

471. The **magnetic oxide** of iron (Fe_3O_4) occurs native. It is the richest of the ores of iron, and when pure contains about 72 per cent of iron.

472. **Ferrous and Ferric Salts.** — There are, generally speak-

ing, two series of iron salts, in one of which the atom **Fe** is **bivalent,** and in the other of which the double atom (Fe_2) is **sexivalent.** Thus there are two chlorides, — ferrous chloride, $FeCl_2$, and ferric chloride, $(Fe_2)Cl_6$; similarly there are two nitrates, two sulphates, etc.

473. **Ferrous Sulphate** ($FeSO_4$). — A hydrate of this compound, of composition $FeSO_4 + 7\,H_2O$, usually called *copperas* or *green vitriol*, is the most common of all the compounds of iron. It may readily be prepared by dissolving metallic iron or ferrous sulphide in dilute sulphuric acid. On the large scale it is commonly prepared by roasting iron pyrites (FeS_2) at a gentle heat.

When perfectly pure, the crystals of **ferrous sulphate** are compact, transparent and of a bluish-green color; but in dry air they effloresce and become covered with a white incrustation, the color of which subsequently changes to rusty brown through absorption of oxygen. The common commercial article is of a grass-green color, and is contaminated with more or less ferric sulphate. When heated, the crystals first lose their water of crystallization, and on further application of heat the salt is decomposed, sulphurous and sulphuric anhydrides are given off, while ferric oxide remains. Upon this fact depends the preparation of fuming sulphuric acid (§ **135**).

474. **Ferric sulphate** ($Fe_2\,3\,SO_4$) is interesting, chiefly from its analogy with aluminum sulphate. Like the aluminum salt, it combines with the sulphates of the alkali-metals, to form well-defined **alums.**

475. When exposed to the air, or to oxidizing agents, the **ferrous salts** have a great tendency to absorb oxygen.

Exp. 212. — Pour a solution of copperas into an open capsule, and leave it exposed to the air for a day or two; the solution will gradually become yellow as the oxidation proceeds, and after a while a rusty precipitate of ferric oxide, or of highly basic ferric sulphate, will fall.

Exp. 213. — Dip a small piece of cotton cloth in the solution of nutgalls prepared in Exp. 151, and allow it to become dry; then dip

it in the solution of copperas and hang it up in damp air. Black, insoluble iron tannate will be so firmly precipitated in and upon the fibres of the cloth, that it cannot be washed away.

This experiment illustrates one general method of dyeing, by means of which blacks and grays of various shades may be applied to cloth or leather, though in practice other astringent dye-stuffs, such as catechu, cutch or gambier, are commonly employed in place of nutgalls.

Ferrous sulphate is largely employed in dyeing, sometimes directly, as in the foregoing experiment, but often as the source of other compounds of iron, which are employed as mordants ; ferrous acetate, for example, obtained by decomposing ferrous sulphate with calcium acetate, is a compound much used by dyers. It should be remarked, however, that ferrous acetate is sometimes made directly by dissolving scraps of iron in vinegar or pyroligneous acid (§ 238). Ferrous sulphate is also used in dyeing with indigo. Its use depends upon the fact, that, when a solution of copperas is treated with calcium hydrate, a ferrous hydrate is precipitated ; this ferrous hydrate has such a tendency to absorb oxygen, that a mixture of copperas and slaked-lime forms a powerful reducing mixture.

Exp. 214. — Dissolve 1 grm. of copperas (iron sulphate) in 100 c. c. of water in a bottle of 200 c. c capacity. Into the solution stir a mixture of 1 grm. of finely powdered indigo and 1.5 grms. of freshly slaked lime ; fill up the bottle with water and cork it. Shake the bottle occasionally, and, after eight or ten hours, pour off, or remove with a pipette (Appendix, § 20), a portion of the clear and nearly colorless liquid without disturbing the precipitate in the bottom of the bottle. Expose this liquid to the air in a shallow dish ; it contains white indigo in solution, but the oxygen of the air rapidly causes the formation of blue indigo insoluble in the liquid, as was seen in Exps. 159, 160, § 342, where a different reducing agent was employed.

476. **Silicates of Iron.** — Several native silicates of iron are known, but none of them are of special interest. The green tinge of ordinary glass is due to the presence of a **ferrous silicate,** and by increasing the proportion of the ferrous salt, a deep bottle-green color may be imparted to the glass. This color may be destroyed by introducing into the glass during the manufacture manganese binoxide, or some other oxidizing agent. The ferrous silicate is thus converted into **ferric silicate** which has little coloring power.

477. **Cyanides of Iron.** — There is a **ferrous cyanide** ($Fe(CN)_2$), known as a yellowish-red precipitate, which takes up oxygen and becomes blue when exposed to the air, and a **ferric cyanide** ($Fe_2(CN)_6$) has been obtained in solution. But by far the best known of the cyanides of iron are certain double compounds, which constitute the familiar pigments, known, collectively, as **Prussian blue.** Common Prussian blue ($Fe_7C_{18}N_{18} + 18\ H_2O$), may be regarded as a compound of ferrous and ferric cyanides, $3\ Fe(CN)_2, 2\ (Fe_2(CN)_6) + 18\ H_2O$; it may be prepared as follows : —

Exp. 215. — Add to an exceedingly dilute solution of almost any ferric salt, such, for example, as the ferric sulphate of Exp. 211, a drop of potassium ferrocyanide (§ 387). A beautiful blue precipitate will form, and will remain suspended in the liquor for a long while. Another variety of Prussian blue, known as *Turnbull's blue*, may be obtained by mixing a solution of potassium ferricyanide (§ 388) with a solution of copperas or other ferrous salt.

Since potassium ferrocyanide will give no blue coloration with ferrous salts, and since the ferricyanide yields no blue with ferric salts, it is evident that the two solutions may be used as **tests** by which to detect the presence of ferrous and ferric salts, respectively, in any solution.

Exp. 216. — Soak a piece of cotton cloth in a solution of ferric sulphate (Exp. 211), and then immerse it in an acidulated solution of potassium ferrocyanide. Prussian blue will be precipitated upon the cloth, and will remain firmly attached to it. Prussian blue is largely employed in dyeing and calico printing in a variety of ways.

478. **Iron protosulphide** (FeS) is a substance of great value to the chemist as the cheapest source of the important reagent, **sulphuretted hydrogen** (§ 121). The sulphide may be prepared by igniting pyrites in a covered crucible, by rubbing roll brimstone against a white hot iron bar, or by fusing together sulphur and iron turnings (**Exp. 47, § 115**).

Exp. 217. — Dissolve a small crystal of ferrous sulphate (copperas) in water, and add to the liquid a drop or two of ammonium sulphydrate (§ 401). Black iron sulphide will be thrown down. The finely divided protosulphide thus obtained in the wet way, dis-

solves much more quickly in acids than the compact sulphide obtained by the way of fusion ; in contact with acids it evolves gas so tumultuously that it would be inconvenient as a source of hydrogen sulphide. The black earth between the stones of the pavements of cities, and at the bottom of drains and cesspools, owes its color to iron protosulphide formed by the putrefaction of sulphuretted compounds in contact with ferric oxide contained in the earth.

479. **Iron bisulphide** (FeS_2) occurs abundantly in nature as the well-known mineral **iron pyrites.** When the pyrites is roasted at a high temperature, sulphurous anhydride is formed, and ferric oxide left, as in the manufacture of sulphuric acid. When the temperature of the burning pyrites is kept low, the product is principally ferrous sulphate, and a large amount of copperas is thus obtained by roasting pyrites and then treating with water. Under certain conditions pyrites oxidizes in the air at the ordinary temperature ; the **spontaneous combustion** of many kinds of coal is due to the oxidation of iron pyrites disseminated through the combustible.

COBALT (Co) AND NICKEL (Ni).

480. **Cobalt** and **nickel** are two metals remarkably similar to each other in both physical and chemical properties. They occur together in nature, generally in combination with sulphur and arsenic. They have the same atomic weight (58.8) and nearly the same specific gravity (8.2 to 8.9). Nickel is somewhat used as an ingredient of certain alloys, of which German silver, composed of copper, zinc and nickel, is the most familiar.

Like iron, cobalt and nickel form protoxides (**CoO** and **NiO**) and corresponding proto-salts ; like iron, they form sesquioxides (Co_2O_3 and Ni_2O_3) and corresponding per-salts. Unlike iron, however, the protoxides are more stable compounds than the sesquioxides. To designate the two series of salts, the terms *cobaltous* and *cobaltic*, *nickelous* and *nickelic* are sometimes employed.

481. **The Sesquioxide Group.** — The most striking characteristic of the metals which have been grouped together in this chapter is the property which they possess of forming **sesquioxides** and a corresponding series of salts ; most of them

form protoxides as well, and if we arrange the metals in the order of their atomic weights,

Gl = 14, Al = 27.4, Cr = 52.5, Mn = 55, Fe = 56, Ni = 58.8, Co = 58.8,

the sesquioxides of the metals at the head of the list are the most stable of the sesquioxides, and the protoxides of nickel and cobalt are the most stable of the protoxides, while with manganese and iron both forms of oxide are well represented. Glucinum and aluminum have no protoxides at all, and the protoxide of chromium is very unstable.

482. **Uranium** (**Ur**) (at. wt. = 120). — With the members of this group may be classed the rare metal uranium, the sesquioxide of which is used to give a beautiful yellowish-green color to glass, and also the following elements, which are more or less nearly related to aluminum and iron:—Yttrium, **Yt**; Erbium, **Er**; Cerium, **Ce**; Lanthanum **La**; Didymium, **Di**; Gallium, **Ga.**

CHAPTER XXVII.

COPPER AND MERCURY.

COPPER (Cu).

483. Though by no means one of the most abundant metals, **copper** is nevertheless very widely diffused in nature, and is largely employed by man. Traces of it exist in almost every soil, whence it is taken up by plants, in which it may almost always be detected by refined testing. Traces of it have repeatedly been found also in the various animal organs and secretions. Besides occurring in the native state, copper is found in a great variety of combinations; the most common of its ores, however, is the sulphide, or rather a compound of copper sulphide and iron sulphide in varying proportions, known as copper pyrites. The carbonates and oxides of copper are also valuable as ores.

484. **Copper** is a rather hard metal, of a well-known red color; it is very tenacious, ductile and malleable. At the ordinary temperature the metal is not altered in dry or moist air, unless finely divided. When heated in the air it becomes covered with a coating of a black oxide. Metallic copper is not very readily acted upon by acids, excepting those rich in oxygen. Except when finely divided it is scarcely acted upon by even concentrated chlorhydric acid; in hot sulphuric acid it dissolves as copper sulphate, sulphurous anhydride being given off; in nitric acid somewhat diluted, it dissolves readily as copper nitrate, and nitric oxide escapes (**Exp. 19, § 50**).

485. Several of the compounds of copper with other metals are of great importance in the arts. Brass and the yellow-metal used for sheathing ships are alloys of zinc and copper; bronze, gun-metal and bell-metal are alloys of tin and copper, and various *compositions* are produced by mixing these alloys with brass; copper is also an essential ingredient of all the common coins, implements and ornaments of gold and silver.

486. **Cuprous and Cupric Salts.** — There are two series of copper salts, in one of which the atom **Cu** is **bivalent**, while in the other the double atom Cu_2 is **bivalent**. Thus, cupric chloride is $CuCl_2$; cuprous chloride is Cu_2Cl_2. As a rule the cupric salts are the more common and the more stable of the two series.

487. **Oxides of Copper.** — There are two oxides of copper. **Copper suboxide, cuprous oxide** or **red oxide of copper** (Cu_2O) occurs in nature as "*ruby copper*." It may be prepared artificially in various ways, as, for example, by the action of certain reducing agents on alkaline solutions of cupric salts (**Exp. 135, § 298**). Cuprous oxide is used to give a ruby-red color to glass. **Copper oxide, cupric oxide** or **black oxide of copper** (**CuO**) may be prepared by heating the metal in a current of air, or by igniting the carbonate, hydrate or nitrate.

Exp. 218. — Bind a bright copper coin with wire, in such manner that a strip of wire 8 or 10 c. m. long shall be left projecting from the coin; thrust the free end of the wire into a long cork or bit of

wood, and by means of this handle hold the coin obliquely in a small flame of the gas-lamp. A beautiful play of iridescent colors will appear upon the surface of the copper, particularly if it be moved to and fro. Thrust the hot coin into water, and observe that it is at this stage covered with a red coating of copper suboxide. Replace the coin in the lamp and hold it in the hot oxidizing portion of the flame; it will soon become black from the formation of copper protoxide. After a rather thick coating of oxide has been formed, again quench the coin in water: the black coating or scale of oxide will fall off, and beneath it will be seen a thin film of the suboxide firmly adhering to the metal.

Exp. 219. — Evaporate to dryness in a porcelain dish upon a sand-bath some of a solution of copper nitrate prepared from copper, as in Exp. 21. Place a small quantity of the dry residue upon a fragment of porcelain, and ignite it until red nitrous fumes are no longer given off. Copper protoxide will be left upon the porcelain.

488. **Copper hydrate** (CuH_2O_2) is formed when caustic alkali is added to a solution of a salt of copper.

Exp. 220. — Place in a test-tube, or small bottle, 8 or 10 c. c. of a cold dilute solution of copper sulphate, and add to it enough of a solution of caustic soda to render the mixture alkaline to test-paper. A light blue precipitate will fall; hydrate of copper is insoluble in water and in soda lye.

Exp. 221. — Repeat Exp. 220, with the difference that the solutions of caustic soda and copper sulphate are both heated to boiling, and are mixed while hot. Instead of the blue hydrate, black copper protoxide will now be thrown down, for copper hydrate readily parts with its water when heated, even if it be all the while immersed in water; it does not again combine with water after it has become cold.

Exp. 222. — Again repeat Exp. 220, but instead of soda lye add to the copper salt ammonia-water, drop by drop, and shake the tube after each addition of the ammonia. Copper hydrate will be precipitated as before in accordance with the reaction,

$$CuSO_4 + 2\,(NH_4)HO = (NH_4)_2SO_4 + CuH_2O_2,$$

for, as has been said, this hydrate is insoluble in water; but since copper hydrate is readily soluble in ammonia-water, the precipitate will redissolve as soon as more of this agent than is needed to decompose the copper salt is added. The ammoniacal solution of copper has a magnificent azure-blue color.

489. **Copper sulphate** ($CuSO_4$) may be obtained by treating metallic copper with hot sulphuric acid (see § **123**), or by dissolving copper oxide in dilute sulphuric acid. The salt crystallizes with 5 equivalents of water. This hydrated salt is known as **blue vitriol,** and is much used in the arts.

It is remarkable that the blue color of copper sulphate depends upon the presence of water.

Exp. 223. — Heat a little powdered blue copper sulphate upon a piece of porcelain ; as it loses its water, the light-blue powder will turn white. A drop of water upon the anhydrous powder will restore the blue color.

490. **Acetates of copper** are formed by the action of acetic acid upon metallic copper exposed to the air. They are commonly called **verdigris.** Verdigris is usually prepared by packing plates of copper between woollen cloths steeped in vinegar. The term is often, although incorrectly, applied to the green coating of carbonate which forms on metallic copper when long exposed to moist air.

Sulphides of copper (Cu_2S and CuS) occur native, and the double sulphide of copper and iron called copper pyrites has already been mentioned as an ore of copper. **Cupric sulphide** (CuS) is of considerable importance to the analyst ; it is formed when hydrogen sulphide is passed into a solution of a cupric salt, and is a black powder, insoluble in water, in dilute acids, and in alkaline solutions.

MERCURY (Hg).

491. Small globules of metallic **mercury** are sometimes found in nature ; but the principal ore of this metal is the sulphide HgS, called **cinnabar.** From this sulphide the metal is readily extracted by distilling a mixture of it and quicklime, or iron-turnings, in cast-iron retorts. The sulphur is retained by the lime, or iron, as the case may be, while metallic mercury passes off in the state of vapor into receivers containing water, beneath which it condenses to the liquid state. Large quantities of mercury are used in extracting gold and silver from

their ores, for silvering mirrors, and in the process of fire-gilding. Preparations of mercury are employed also as medicaments, and for various purposes in the useful arts. The fluidity of the metal makes it valuable in the construction of certain philosophical instruments, of which the thermometer and barometer are familiar examples.

492. At the ordinary temperature of the air **mercury** is a brilliant, mobile liquid, of 13.6 specific gravity; it freezes at — 39.4°, becoming a ductile solid of tin-white color and granular fracture, which can be cut with a knife. Mercury vaporizes slowly, even at ordinary temperatures, and boils at about 360°. The specific gravity of mercury vapor is 100, its atomic weight 200. The symbol **Hg** thus denotes the two-volume weight of this element (§ 140), and the molecule of mercury is regarded as containing but a single atom.

493. **Pure mercury** is unacted upon by the air at the ordinary temperature; when heated it is converted into the **red oxide.** It is not attacked by chlorhydric acid; hot sulphuric acid converts it into mercury sulphate; it dissolves readily in nitric acid.

494. **Compounds of Mercury.** — There are two **oxides** of mercury, — an unstable black **suboxide** (Hg_2O) and the ordinary red **mercury oxide** (HgO). This latter oxide, as commonly prepared by heating mercury in the air, or by gently heating mercury nitrate, is a compact, granular, almost crystalline, glistening powder, of bright brick-red color; but when prepared in the wet way by adding caustic alkali to a solution of a mercuric salt, it is, when dry, a soft, orange-colored powder. Mercury oxide is decomposed by heat, as has already been seen (**Exp. 3, § 9**). Corresponding to the oxides of mercury are two series of compounds, the **mercuric** salts in which the atom **Hg** is **bivalent,** and the **mercurous** salts in which the double atom Hg_2 is **bivalent.**

495. **Mercuric sulphide** (HgS), which occurs native as **cinnabar,** is the most important ore of mercury. An artificial product of the same composition, known as **vermilion,** is used as a

pigment. The same compound is formed when hydrogen sulphide is passed into a solution of a mercuric salt; thus prepared it is of a black color. It is insoluble in water, in dilute acids, and nearly insoluble in alkaline liquids.

496. **Mercurous chloride** (Hg_2Cl_2), commonly called **calomel,** is extensively used as a medicament. It is a heavy white powder, which volatilizes at temperatures below redness without previous fusion. It is tasteless, odorless, and as good as insoluble in water.

497. **Mercuric chloride** ($HgCl_2$), better known by the name of **corrosive sublimate,** commonly occurs in commerce, in translucent, crystalline masses. It melts at about 265°, forming a colorless liquid, which boils at 293°; the fumes are acrid, and, like the salt itself, exceedingly poisonous.

Mercuric chloride unites with many organic substances to form compounds insoluble in water and imputrescible. It coagulates albumin, for example, and the more perishable portions of wood; hence the employment of raw white of egg as an antidote in cases of poisoning by corrosive sublimate, and the use of the mercury salt for preserving wood, — a purpose for which it would, no doubt, be largely employed were it not for its high cost. Collections of dried plants, and of other objects of natural history, are preserved both from decay and from the attacks of insects by brushing over them a solution of the chloride in alcohol.

498. **Amalgams.** — Mercury unites with most of the other metals to form alloys, many of which are pasty, or even liquid, when the proportion of mercury contained in them is large. These alloys are commonly called **amalgams,** in contradistinction to the ordinary solid alloys of the other metals, in which mercury has no place. The liquid amalgams are true solutions of other metals, or of solid amalgams, in the fluid mercury. The so-called silvering of mirrors is an amalgam of tin.

Mercury may be detected in almost any soluble salt of the element by introducing into a solution of the salt a piece of clean copper.

Exp. 224. — Place a drop of a solution of either of the nitrates or chlorides of mercury upon a copper coin and rub the liquid over its surface. A white coating of metallic mercury will be deposited upon the metal.

CHAPTER XXVIII.

TIN (Sn).

499. Though by no means widely diffused in nature, and though ores of it occur in but few localities, **tin** is one of the metals which have longest been known to man. The principal ore of tin is the **binoxide,** called **tin-stone.** In order to extract the metal from it, the tin-stone is mixed with powdered coal, and heated upon the hearth of a reverberatory furnace in a reducing flame. The reduced metal melts readily, and is then run out of the furnace into iron moulds.

Tin is a lustrous white metal, soft, malleable and ductile, though not very tenacious. Its ductility varies greatly with the temperature; at 100° the metal may be drawn into thin wire, but at 200° it is very brittle. When a bar of tin is bent it emits a peculiar crackling sound, and if the bending be repeated the metal becomes decidedly warm. These phenomena appear to depend on the disturbance of interlaced crystals contained in the bar, and upon the friction of these crystals one against the other. Tin always exhibits a great tendency to assume the crystalline form in passing from the liquid to the solid condition. Upon this peculiarity is founded a method of ornamenting tinned iron.

Exp. 225. — Heat a piece of common tinned iron over the gas lamp until the tin has melted, thrust the plate into cold water in order that the tin may harden quickly, then remove the smooth surface of the metal by rubbing it first with a bit of paper moistened with dilute aqua regia, and then with paper wet with soda-lye. By this treatment there will soon be laid bare a new surface covered with beautiful crystalline figures, like frost upon a window-pane.

500. **Tin** does not tarnish in the air at ordinary temperatures, and for this reason, as well as on account of its brilliant lustre, tin is largely employed for coating other metals, — copper, for example, as in ordinary pins, cooking vessels and bath-tubs, — and iron, as in common sheet-tin, of which the so-called tin-ware is manufactured.

501. The **alloys** of tin are important. The composition of bronze, bell-metal, etc., has been already mentioned under copper (§ **485**), and that of stereotype metal under antimony (§ **165**). Of the other alloys of tin those formed by its union with lead are most remarkable. *Plumbers' solder* consists commonly of equal parts of lead and tin, though some kinds of it contain only one-third their weight of lead, and others only one-third their weight of tin. *Pewter* is composed of tin, together with a small proportion of lead, and sometimes antimony.

502. **Compounds of Tin.** — There are two oxides of tin, — **tin protoxide** (**SnO**) and **tin binoxide** (**SnO_2**). The latter occurs native, and is the principal ore of tin, as already stated. The binoxide may be prepared in the hydrated form, and is known as **stannic acid.** Sodium stannate is used in dyeing. **Tin bisulphide** (**SnS_2**) is a bright golden-yellow powder known as **mosaic gold,** and used in decorative painting. The **chlorides** of tin (**$SnCl_2$** and **$SnCl_4$**) are the most important of the compounds of tin, and are much used in dyeing.

CHAPTER XXIX.

GOLD AND PLATINUM.

GOLD (Au).

503. Though generally found only in small quantities, **gold** is very widely diffused upon the surface of the globe. Traces of it may be found beneath the sandy beds of most rivers, and it occurs in many of the crystalline rocks and in the soils result-

ing from their decomposition. Many varieties of iron pyrites in particular contain appreciable quantities of gold, and silver is never found in nature altogether free from it. The chief source of the metal as an article of commerce is **native gold**; this is sometimes found in a condition of purity, but is usually alloyed with more or less silver. It is collected, either directly by mechanically washing away the lighter substances with which it is associated, or, in the case of poorer ores, the gold is dissolved out chemically by means of quicksilver, and is subsequently recovered from the amalgam by filtration and distillation.

504. **Pure gold** is remarkable as being the most malleable of the metals. Its softness is nearly as great as that of lead. It has, however, much tenacity, and may be drawn into extremely fine wire; 1 grm. of gold can be made to yield as much as 3 kilometres of wire. The metal can be beaten into leaves which are not more than $\frac{1}{10,000}$ of a millimetre thick. The specific gravity of gold is about 19.3; its atomic weight is 196.

505. In the air, **gold** undergoes no change at temperatures lower than its melting-point; and upon this fact, taken in connection with the beautiful color and lustre of the metal, and its comparative rarity, its principal uses depend.

On account of this indestructibility, gold was regarded by the earlier chemists as the **king of metals**; together with platinum and silver it is still spoken of as a **noble metal.** Few chemical agents, excepting melted metals, have any action upon gold. None of the common acids, when taken singly, can dissolve it, though the metal is completely soluble in a mixture of chlorhydric and nitric acids (§ **75**), and is not completely insoluble in nitric acid contaminated with nitrous acid or with nitrogen peroxide. The elements chlorine and bromine, however, unite with it in the cold, and when hot it is attacked by phosphorus and arsenic.

506. **Alloys of Gold.** — **Gold** unites with most of the other metals; but its most important alloys are those with copper, silver, and mercury. Pure gold is so soft that articles of jew-

elry made of it would quickly wear out if used; such articles, as well as coins and watches, are therefore always made of gold which has been alloyed with copper, in order to increase its hardness. The standard alloy for coin in this country and in France is nine parts by weight of gold to one part of copper; in England it is eleven parts of gold to one of copper.

507. **Salts of Gold.** — The compounds of gold have little chemical interest; two oxides are known (Au_2O and Au_2O_3); the chloride ($AuCl_3$) is somewhat used in the chemical laboratory; and the cyanide or rather a solution of gold cyanide in potassium cyanide is used in electro-gilding.

PLATINUM (Pt).

508. **Platinum** is a metal which, like gold, has little affinity for the other chemical elements. It is commonly found in the native state, alloyed with gold and with other metals. Like gold, it is obtained by washing away the earth and sand with which it is found mixed. It is a very heavy metal, the specific gravity of cast-platinum being 21.15. Its atomic weight is 194.5. The color of platinum is intermediate between the white of silver and the gray of steel; its lustre is far less brilliant than that of silver. It is as soft as copper, very malleable and very tenacious; it may be drawn into wire so fine that its diameter is only $\frac{1}{1200}$ of a millimetre. It is not fusible in ordinary furnaces, but may be used in the blowpipe flame, and is nowadays melted in considerable quantities in lime crucibles by means of a blowpipe flame obtained from common coal-gas and oxygen.

509. **Platinum** does not oxidize in the air at any temperature, nor is it attacked by any of the common acids taken separately; in *aqua regia* (§ **75**) it dissolves slowly, — much less readily than gold. Chlorine-water dissolves it, but neither bromine nor iodine has any action upon it.

From its comparative inertness as a chemical agent, taken in connection with its infusibility, platinum is an extremely useful metal to the chemist. It is employed in the scientific laboratory

for crucibles, evaporating dishes, stills, tubes, spatulæ, forceps, wire, blowpipe tips, and the like; and in the manufacture of oil of vitriol, large platinum stills, together with cooling siphons of the same metal, are employed in the process of concentrating the acid.

With most of the other metals platinum unites readily, forming **alloys** which in many instances are more fusible than platinum itself; hence, in employing platinum vessels in chemical experiments, care must be taken never to touch the platinum with easily fusible metals, or to place in the vessels any easily reducible compound of a metal.

510. A remarkable property of platinum is that of inducing various gases to combine chemically one with the other. This power of causing combination is possessed even by clean surfaces of the ordinary solid metal, though to a much greater degree by spongy platinum (**Exp. 228**), and still more by the very finely divided powder known as **platinum black.**

Exp. 226. — Cut half a gramme, or more, of worn-out platinum foil, or wire, into small fragments, and boil them with a teaspoonful of aqua regia so long as the metal appears to be acted upon, then decant the liquid into a porcelain dish, add to the fragments of platinum another teaspoonful of aqua regia, and proceed as before, repeating the treatment until all the metal has dissolved. By the repeated action of successive small portions of the solvent, platinum and other comparatively insoluble substances can be dissolved much more readily than if all the liquid necessary for its solution were added at once. Evaporate the solution to dryness upon a water-bath, take up the residue with water, and preserve the solution of platinum chloride ($PtCl_4$) thus obtained in a bottle provided with a glass stopper.

Exp. 227. — Pour a teaspoonful of a solution of ammonium chloride into a test-tube, acidulate the liquid with chlorhydric acid, and add to it a drop of the solution of the platinum chloride obtained in the preceding experiment. A yellow, insoluble powder will soon be precipitated. The composition of this precipitate may be represented by the formula $2\,NH_4Cl, PtCl_4$. Repeat the experiment, and this time take enough of the platinum solution and of the ammonium chloride to make half a teaspoonful of the yellow precipitate, taking care that at last there shall be a slight excess of free ammonium chloride rather than of platinum chloride in the supernatant liquid. Allow the precipitate to settle, separate it from the clear liquor by

decantation, and dry it partially at a gentle heat. When the precipitate has acquired the consistence of slightly moistened earth, transfer it to a cup-shaped piece of platinum foil, and heat it to redness in the gas flame, as long as fumes of ammonium chloride continue to escape. All the chlorine, hydrogen, and nitrogen will be driven off, and there will remain upon the foil a gray, loosely-coherent, sponge-like mass of metallic platinum ; it is called *platinum sponge*.

Exp. 228.—Hold the dry platinum sponge of Exp. 227 in a stream of hydrogen or of common illuminating gas issuing from a fine jet. The metal will soon begin to glow, and in a moment will become hot enough to inflame the mixture of air and gas in contact with it. Before friction-matches were employed, this property of spongy platinum, of inflaming hydrogen, was sometimes made use of for striking a light. The mode of action of the platinum in this experiment is obscure ; it has already been alluded to in § 127.

511. **Platinum black** is a term applied to metallic platinum, even more finely divided than the sponge above described. Platinum black is not only capable of absorbing and storing up many times its own bulk of oxygen gas, but it is also capable of giving away this oxygen to many other substances. If easily oxidizable liquids, such as alcohol or ether, are dropped upon platinum black which has previously been exposed to the air, the liquids will be oxidized and converted into new substances, while the powder becomes red-hot from the heat evolved during the act of oxidation.

512. With gold and platinum are classed several rare metals, which are never found except in association with platinum, and which closely resemble that metal. They are commonly called **platinum metals**, and the group may be appropiately termed the **platinum group**. The whole group consists of Rhodium (atomic weight = 104), Ruthenium (104), Palladium (106.5), Gold (196), Platinum (194.5), Iridium (192.7), and Osmium (199). Palladium is used to impart to brass gas-fixtures a peculiar reddish tint, sometimes called salmon-bronze. Iridium is used for the very hard tips of gold pens. Osmium forms, among other oxides, a volatile compound OsO_4, whose vapors are intensely poisonous. The metals of this group are noble metals ; they withstand the action of the atmosphere ; none of them are acted upon by nitric acid, though they dissolve in chlorine and in aqua regia. Their oxides part with all their oxygen when simply heated, leaving the metal behind.

513. **Equivalent Weights.** — In experiments like Exp. 204, § 442, where one metal replaces another, it is found that the replacement always occurs in fixed and definite proportions. In this particular experiment the amount of lead deposited was to the amount of zinc dissolved as 103.5 to 32.5. If a solution of a salt of silver had been employed instead of the lead acetate, the amount of silver deposited would have been to the zinc dissolved as 108 to 32.5. The weights of the metals thus deposited or dissolved, that is to say, the amounts indicated by the numbers 103.5 and 32.5 in the case of lead and zinc, may be said to be the *equivalents* of each other; these numbers (or others bearing the same relation to each other) may be called the *equivalent weights* of lead and zinc respectively. The number of elements whose equivalent weights can be thus determined by the actual replacement of one by the other is limited, but even in cases where two elements do not replace each other, their equivalent weights may still be determined by comparing each of the two elements with a third. In this way, by direct or by indirect means, we may draw up a table of the "equivalent weights" of the different elements; these equivalent weights would be either the same as the atomic weights, or some simple multiple or submultiple of them, for by the very conception of the atomic theory no replacement could take place except by a certain number of whole atoms.

In many works on chemistry the student will find assigned to several of the chemical elements other weights than those given on page 295. Thus, it was customary at one time to assign the weight 16 to sulphur instead of 32, 8 to oxygen instead of 16, etc. These weights are the equivalent weights just described, and they are still often used by persons devoted to the practical applications of chemistry. The reasons which have led to the adoption of the series of atomic weights in present use cannot be appropriately discussed in this manual.* For most purposes of calculation it is immaterial whether the "equivalent" or the "atomic" weights be employed. Thus water is made up of 1 part by weight of hydrogen for 8 parts by weight of oxygen; and it was formerly the custom to represent the equivalent weight of oxygen (8) by the symbol **O**. On this system the symbol **HO** stood for water, and indicated that water contains hydrogen and oxygen in the proportion of 1 to 8, and that its equivalent weight is 9. But since the molecule of water is held to contain two atoms of hydrogen

* The subject is discussed with more or less fulness in most of the larger text-books of chemistry.

and one atom of oxygen, the atom of oxygen weighing 16, the symbol of the compound is written H_2O. The proportion of hydrogen to oxygen is in both cases the same ; and, in general, it is evident that the relative proportion in which any two or more elements exist in a chemical compound is a matter of fact determined by analysis : it is something which no theoretical conceptions of ours can change. The atomic weights, however, or the values which we assign to the symbols of the elements, must be fixed by what we hold to be true with regard to the number of atoms in the molecule of the compound. It is a better knowledge of the molecular constitution of bodies than was accessible to their predecessors that has led the chemists of the present day to employ new atomic weights in the case of a considerable number of the elements. The more common elements whose atomic weights are double the equivalent weights formerly assigned to them are as follows : —

Aluminum,	Iron,	Platinum,
Barium,	Lead,	Selenium,
Cadmium,	Magnesium,	Silicon,
Calcium,	Manganese,	Strontium,
Carbon,	Mercury,	Sulphur,
Chromium,	Nickel,	Tin,
Cobalt,	Oxygen,	Uranium,
Copper,	Palladium,	Zinc.

In passing, then, from the formulæ of the older system to the corresponding formulæ of the new, if the atomic weight of any element is double the old equivalent weight, it becomes necessary, in writing the symbol of any molecule containing this element, either to take half as many atoms of the element in question or to take twice as many atoms of the other elements in the molecule unless they also have had their combining weights doubled. Thus the symbol of the stannic chloride was formerly written $SnCl_2$; now, since the atomic weight of tin is 118 while the old equivalent weight was 59, the symbol must be written $SnCl_4$, in order to express the same relative proportion of chlorine and tin.

514. **Nomenclature.** — In connection with the adoption of the atomic weights now in use, although not logically dependent upon it, there have occurred certain changes of nomenclature, especially in regard to the salts of the ordinary acids. The term acid itself is not used in the same sense as formerly. Now (see pages 41 – 43) we are inclined to restrict the term acid to bodies containing hydrogen which

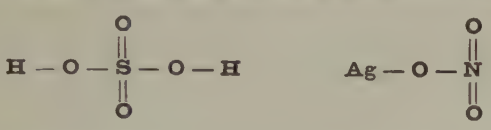
can be replaced by a metallic element ; it was formerly applied also to bodies which in this book have been called anhydrides. Thus SO_3 was called sulphuric acid (or anhydrous sulphuric acid), and H_2SO_4 was regarded as a compound of SO_3 and water, and written H_2O, SO_3. In like manner the sulphates were regarded as compounds of SO_3 with the oxides of the metallic elements, and were named, in accordance with this idea, sulphate of soda, sulphate of lime, etc., instead of sulphate of sodium, sulphate of calcium, etc. There is at the present time, however, no uniformity of nomenclature. Some chemists say sulphate of sodium, some say sodium sulphate, others say sodic sulphate ; while the old term sulphate of soda contends with them and with the still older term, Glauber's salt, for a place in the language of commerce, of literature, and of ordinary life. As a rule, when there are two series of salts derived from the same element, it is usual to distinguish between the two by the use of the terminations *-ous* and *-ic*, as, for example, ferr*ous* sulphate and ferr*ic* sulphate.

In the designation of the so-called binary compounds (*i. e.* compounds of two elements only) there is the same diversity of practice ; thus the names soda, oxide of sodium, sodium oxide, and sodic oxide are all applied to the same compound of oxygen and sodium. Where there are two oxides of the same element (or chlorides, sulphides, etc.), the terminations *-ous* and *-ic* are sometimes employed ; more generally, however, prefixes, either Latin or Greek, are used : thus, when the molecule of an oxide contains only one atom of oxygen it is called the *protoxide* or *monoxide ;* when there are two atoms of oxygen in the molecule, it is called the *binoxide* or *di-oxide* ; succeeding compounds would be the *teroxide* or *trioxide*, *quadroxide* or *tetroxide*, etc. (see page 37).

515. **Quantivalence.**—In addition to the statements of § 74, it may be remarked that the atom of the same element does not always possess the same quantivalence. Thus, while the quantivalence of hydrogen is always taken as 1, and that of oxygen as 2, the quantivalence of sulphur is sometimes 6, sometimes 4, and sometimes 2, that of nitrogen is sometimes 5 and sometimes 3. As a rule, when an element varies in quantivalence, the various degrees of quantivalence possible to the same atom are either all odd or all even.

We do not know to what the observed difference in the combining power of the different atoms is due. In order, however, to represent it to the eye, it is usual to attach to the symbol of the atom of an element as many dashes as will indicate the quantivalence. If com-

bination takes place between elementary atoms of two kinds, the *total quantivalence* of each element must be the same. If this be expressed graphically, the number of dashes attached to each symbol, or, as is often said, the number of *bonds* must be the same. Thus, in **H — Cl** we have represented the union of 2 univalent atoms; in **H — O — H** the union of one bivalent with two univalent atoms. If a compound is made up of atoms of more than two kinds, it is still possible to write the symbol graphically, so as to represent each atom as united to other atoms by all the bonds attached to it to indicate its quantivalence. Thus, H_2SO_4 and $AgNO_3$ may be written



In these symbols the atoms are represented, **H** and **Ag** as univalent, **O** as bivalent, **N** as quinquivalent, and **S** as sexivalent. No molecule can exist, by this theory, in which the atoms must be represented with bonds unconnected with other atoms: thus there could be no such molecule as **HO**, for if written graphically, **H — O —**, it is seen that the oxygen is "unsatisfied." Such a group of atoms is called a **compound radical**, and the number of bonds unsatisfied is the quantivalence of the radical. Thus **HO —** is a univalent radical, while **H — O — H**, **H — O — O — H** (hydrogen peroxide), **H — O — Ca — O — H** (calcium hydrate) are satisfied or "saturated" molecules. This shows how it is possible for the single atom of copper to be bivalent (**— Cu —**) and for the group of two atoms to form a bivalent combination — (**Cu — Cu**) — . This grouping of the atoms together is not an arbitrary matter of the nature of a "dissected map." In the arrangement of the atoms it is not simply a question of so linking the atoms together that the conditions implied by the quantivalence of the atoms shall be satisfied; such formulæ attempt also to represent in some sense the *structure of the molecule*, at least so far as to indicate the relations which we believe to exist among the various atoms which compose it; this is, however, a matter not sufficiently elementary in its character to be considered in this place. Undue stress is laid upon this matter of quantivalence by many chemists; but the theory expresses, although in a rather crude way, relations which actually exist, and although it

may, and probably will, be displaced by some other theory which will explain the same facts in a more satisfactory manner, it has been, and is, of great value. To the beginner it is chiefly valuable for the aid afforded in writing formulæ and equations. The **graphical formulæ** and equations written in accordance with this theory, are useful, chiefly because they can be made to represent more facts and more suppositions than can be expressed in ordinary formulæ and equations.

The term **atomicity** is applied to the highest degree of quantivalence which the same atom may possess; and the atoms are designated as monads, dyads, triads, tetrads, pentads, hexads and heptads, according as the atomicity is one, two, three, four, five, six, or seven. These terms, monad, dyad, etc., are sometimes used, however, to denote the more common degree of quantivalence, rather than the highest which the atom is capable of exhibiting. Thus the atomicity of lead is four; its prevailing quantivalence is two; lead would thus, according to the first plan, be spoken of as a tetrad, according to the second as a dyad.

516. **Oxidation and Reduction.**—The terms oxidation and reduction are used in a much wider sense than is implied in § 129 on page 81, although the simplest use is as there indicated. As an example of another use of the terms we may take the case of the two chlorides of tin. If by some chemical process the stann*ous* oxide (**SnO**) were converted into the stann*ic* oxide (**SnO_2**), we should legitimately speak of this as a process of oxidation; if, now, the stann*ous* chloride (**$SnCl_2$**) in which the atom of tin, as in stannous oxide, is bivalent, be converted into the stann*ic* chloride (**$SnCl_4$**), in which the atom of tin, as in stannic oxide, is quadrivalent, we speak of this process also as one of oxidation, although there is no oxygen in either compound. If the reverse action were performed, and the stannic chloride were converted into the stannous chloride, we should speak of the process as one of reduction. The ferrous compounds are converted into the ferric compounds, the salts of chromium into chromates, the mercurous salts into mercuric, and so on, by *oxidizing* agents, and, in general, *where an element can occur with two different degrees of quantivalence, the passing from the lower to the higher is brought about by an oxidizing action, the passing from the higher to the lower by a reducing action.* No objection can be made to the use of the terms reduction and reducing agent in this connection; the terms oxidation and oxidizing agent are, in some

cases, manifestly improper, although still often used. Such use of the terms originated when the dualistic idea that the salts *contained* the corresponding oxides was generally accepted, and from such salts as sulphates, etc., the use was extended even to chlorides.

Other characteristic examples of oxidizing and reducing actions are as follows :—

(p. 152) $$\underset{\text{Alcohol.}}{C_2H_5, HO} + O = \underset{\text{Aldehyde.}}{C_2H_3O, H} + H_2O.$$

Here the aldehyde contains no more oxygen than the alcohol, but it contains less hydrogen, a portion of the hydrogen having been oxidized and removed as water.

(p. 200) $$\underset{\text{Indigo blue.}}{C_{16}H_{10}N_2O_2} + H_2 = \underset{\text{Reduced indigo.}}{C_{16}H_{12}N_2O_2}.$$

Here the hydrogen acts as a reducing agent, not by appropriating oxygen, but by actually entering into the molecule. When the reduced or white indigo is exposed to the air it becomes blue. The white indigo is said to be oxidized, although the action is really a removal of hydrogen, as seen in the following equation :—

$$\underset{\text{Reduced indigo.}}{C_{16}H_{12}N_2O_2} + O = \underset{\text{Indigo blue.}}{C_{16}H_{10}N_2O_2} + H_2O.$$

Chlorine is often spoken of as an oxidizing agent ; it acts in two distinct ways, which may be illustrated as follows :—

$$Hg_2Cl_2 + 2\,Cl = 2\,HgCl_2.$$

$$\underset{\text{Arsenious acid.}}{3\,H_2O, As_2O_3} + 2\,H_2O + 4\,Cl = \underset{\text{Arsenic acid.}}{3\,H_2O, As_2O_5} + 4\,HCl.$$

In the first equation chlorine enters into the compound oxidized ; the mercurous chloride is said to be "oxidized" to mercuric chloride. In the second equation the chlorine acts by appropriating the hydrogen of two molecules of water, leaving the oxygen free to enter into combination.

517. **Volumetric interpretation of symbols.**—We have already seen (page 88) that all gaseous molecules are believed, under like conditions, to occupy the same space ; consequently, the symbols for all molecules may be taken to represent equal volumes of the substances indicated, and by general agreement *the symbol of a molecule when used to express volumetric relations always stands for two volumes.* The symbols of the individual elements, as **H**, **O**, **N**, etc., we have already used to represent, 1st, an atom of the element, and 2d, a

certain number of parts by weight of the elementary substance, namely, that number of parts which is indicated by the combining or atomic weight. The same symbol may be also used to denote (3d) a certain *volume* of the element in question, when that element is in the gaseous state. We have already used (page 18 and often) the symbols **H**, **O**, **N**, and **S**, to denote one volume of hydrogen, oxygen, nitrogen and sulphur (vapor), respectively, and, in general, when the element is one whose molecule contains two atoms, the symbol for the atom is used to indicate one volume. When the element is one whose molecule contains only one atom, the symbol for the atom will be also the symbol of the molecule, and will denote two volumes :—thus, **Hg** denotes two volumes of mercury vapor. When the element is one whose molecule contains 4 atoms, the symbol for the atom will indicate only half a volume :—thus, **P** stands for only half a volume of phosphorus vapor. Examples of the volumetric interpretation of symbols are found on pages 34, 37, 46, 97, and others. As the great majority of the known elements cannot be volatilized, or made gaseous, by the highest temperatures as yet at our command, under conditions which permit the chemist to experiment with the gases produced, it is plain that the composition by weight is, in the present state of chemistry, of far greater practical importance than composition by volume.

518. **Coincidence of Atomic Weight and Unit-Volume Weight.**—The specific gravity of a gas or vapor is the weight of any volume of that gas or vapor as compared with the weight of the same volume of hydrogen gas under like conditions of temperature and pressure ; we use the term **vapor density** to denote the same idea, and, less commonly, the term **unit-volume weight.** The same number expresses both the vapor density and the atomic weight in the case of those elements mentioned on p. 91, whose molecules contain each two atoms. Of course, this coincidence is something that is established by experimental observation ; it does not follow from, but actually is a part of the basis of, our theory as to the constitution of the molecules in question. In the case of the elements whose molecules contain four atoms each, the vapor density will be twice the atomic weight, and in the case of the elements whose molecules contain one atom each, the vapor density will be one-half the atomic weight.

It is not necessary to suppose that the same elementary substance

always, and under all conditions, contains the same number of atoms in the molecule. In the first place it is only when the elementary substances are gaseous that we have, at present, means for arguing as to the constitution of their molecules. The molecule of sulphur in the gaseous state contains two atoms, but in the solid state it may contain more than two. In fact, the phenomena of allotropism are best explained by supposing either that the various modifications have a different number of atoms in the molecule, or that there is some difference in the arrangement of these atoms. In the case of ozone there is good reason to suppose that the molecule contains 3 atoms, while the molecule of oxygen contains only 2, as already stated on page 70.

519. **Electrical Relations of the Atoms.**—[To accompany page 257.] Speaking somewhat loosely, all the elements which in this list precede *gold* are negative, while gold and the elements which follow it are positive. We have been in the habit of speaking of the negative elements collectively as the non-metallic elements. The terms negative and positive are, on some accounts, to be preferred, although themselves not perfectly exact in their signification. The same element in different compounds will often play a very different part. Thus the element zinc, which we are now studying, acts in its compounds ordinarily as a positive element; its hydrate (ZnH_2O_2) is a base, its oxide (**ZnO**) is a basic anhydride, and the element when in combination is usually combined with negative elements or radicals, as, for example, in $ZnCl_2$, $ZnSO_4$, etc. Occasionally, however, zinc plays the part of a negative element, as, for instance, in potassium zincate (Exp. 202). In this compound the zinc plays the same part that sulphur does in the sulphates, nitrogen in the nitrates, etc. Corresponding to potassium zincate (K_2O_2Zn), we should have zincic acid (H_2O_2Zn) and zincic anhydride (**ZnO**). In fact, the hydrate of zinc does dissolve, either in acids (acting, therefore, as a base) or in alkalies (acting as an acid). Many of the elements which we generally designate as positive or metallic, act in a similar manner; this difference of action is often accompanied by difference in *quantivalence.* Thus in the case of chromium, we have two very distinct classes of compounds; 1st, the salts of chromium, in which we recognize the double atom of chromium, Cr_2, acting as a hexivalent *positive* radical; 2d, the chromates of various elements in

which the single atom of chromium, **Cr**, is hexivalent and negative. Corresponding to the former of these two classes we have the basic oxide, Cr_2O_3, and the basic hydrate, $Cr_2H_6O_6$; corresponding to the second class we have the acid anhydride CrO_3 and the acid H_2CrO_4.

CHAPTER XXX.

ATOMIC WEIGHTS OF THE ELEMENTS.

In the following list, the names of the rarer elements which are, at present, of little importance, are printed in italics. The discovery of several other elements has been announced but their existence is not yet placed beyond doubt.

Aluminum,	Al	27.4		Mercury,	Hg	200	
Antimony,	Sb	120		*Molybdenum*,	Mo	96	
Arsenic,	As	75		Nickel,	Ni	58.8	
Barium,	Ba	137		Nitrogen,	N	14	
Bismuth,	Bi	210		*Osmium*,	Os	199	
Boron,	B	11		Oxygen,	O	16	
Bromine,	Br	80		*Palladium*,	Pd	106.5	
Cadmium,	Cd	112		Phosphorus,	P	31	
Cæsium,	Cs	133		Platinum,	Pt	194.5	
Calcium,	Ca	40		Potassium,	K	39.1	
Carbon,	C	12		*Rhodium*,	Rh	104	
Cerium,	Ce	*141		*Rubidium*,	Rb	85.7	
Chlorine,	Cl	35.5		*Ruthenium*,	Ru	104	
Chromium,	Cr	52.5		*Selenium*,	Se	79.5	
Cobalt,	Co	58.8		Silicon,	Si	28	
Columbium,	Cb	94		Silver,	Ag	108	
Copper,	Cu	63.4		Sodium,	Na	23	
Didymium,	D	*140		*Strontium*,	Sr	87.5	
Erbium,	E	*167		Sulphur,	S	32	
Fluorine,	F	19		*Tantalum*,	Ta	182	
Glucinum,	Gl	14		*Tellurium*,	Te	128	
Gold,	Au	196		*Thallium*,	Tl	204	
Hydrogen,	H	1		*Thorium*,	Th	231.4	
Indium,	In	113.4		Tin,	Sn	118	
Iodine,	I	127		*Titanium*,	Ti	50	
Iridium,	Ir	192.7		*Tungsten*,	W	184	
Iron,	Fe	56		*Uranium*,	Ur	120	
Lanthanum,	La	*139		*Vanadium*	V	51.3	
Lead,	Pb	207		*Yttrium*,	Yt	*91 ?	
Lithium,	Li	7		Zinc,	Zn	65	
Magnesium,	Mg	24		*Zirconium*,	Zr	89.6	
Manganese,	Mn	55		*Gallium*,	Ga	69.8	

* On the supposition that the principal oxide is a sesquioxide.

In the following list the more important of the elements are arranged in the groups in which they have been studied in the preceding pages. Without accepting any one infallible criterion of classification, or insisting upon any systematic arrangement of the elements in groups with that strenuousness which is apt to make classification rather a hindrance than a help, the student may provisionally use this subdivision of the elements into groups, as a help in remembering facts, as a guide to the prompt recognition of general properties and general laws, and as a suggestive compend of his whole chemical knowledge: —

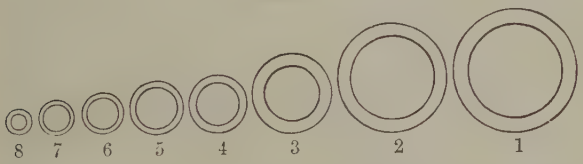
Fluorine,	19	Calcium,	40
Chlorine,	35.5	*Strontium*,	87.5
Bromine,	80	Barium,	137
Iodine,	127	Lead,	207
Oxygen,	16	Magnesium,	24
Sulphur,	32	Zinc,	65
Selenium,	79.5	Cadmium,	112
Tellurium,	128		
		Glucinum,	14
Nitrogen,	14	Aluminum,	27.4
Phosphorus,	31	Chromium,	52.5
Arsenic,	75	Manganese,	55
Antimony,	120	Iron,	56
Bismuth,	210	Cobalt,	58.8
		Nickel,	58.8
Carbon,	12	*Uranium*,	120
Boron,	11		
Silicon,	28	Copper,	63.4
		Mercury,	200
Hydrogen,	1		
Lithium,	7	Tin,	118
Sodium,	23		
Potassium,	39.1	Gold,	196
Silver,	108	Platinum,	194.5

APPENDIX.

CHEMICAL MANIPULATION.

1. Glass-tubing. — Two qualities of glass-tubing are used in chemical experiments, — that which softens readily in the flame of a gas- or spirit-lamp, and that which fuses with extreme difficulty in the flame of the blast-lamp. These two qualities are distinguished by the terms *soft* and *hard* glass. Soft glass may be used for all purposes, except the intense heating, or ignition, of dry substances. Fig. I represents the most convenient sizes of glass-tubing, both hard and soft, and shows also the proper thickness of the glass walls for each size.

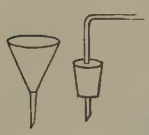
FIG. I.



2. Cutting and Cracking Glass. — Glass-tubing and glass-rod must generally be cut to the length required for any particular apparatus. A sharp triangular file is used for this purpose. The stick of tubing, or rod, to be cut is laid upon a table, and a deep scratch is made with the file at the place where the fracture is to be made. The stick is then grasped with the two hands, one on each side of the

mark, while the thumbs are brought together just at the scratch. By pushing with the thumbs and pulling in the opposite direction with the fingers, the stick is broken squarely at the scratch, just as a stick of candy or a dry twig may be broken. The sharp edges of the fracture should invariably be made smooth, either with a wet file, or by softening the end of the tube or rod in the lamp. (See Appendix, § 3.) Tubes or rods of sizes 4 to 8 inclusive may readily be cut in this manner ; the larger sizes are divided with more difficulty, and it is often necessary to make the file-mark both long and deep. An even fracture is not always to be obtained with large tubes. The lower ends of glass funnels, and those ends of gas delivery-tubes which enter the bottle or flask in which the gas is generated, should be filed off, or ground off on a grindstone, obliquely (Fig. II), to facilitate the dropping of liquids from such extremities.

FIG. II.



In order to cut glass plates, the glazier's diamond must be resorted to. For cutting exceedingly thin glass tubes and other glass ware, like flasks, retorts and bottles, still other means are resorted to, based upon the sudden and unequal application of heat. The process divides itself into two parts, the producing of a crack in the required place, and the subsequent guiding of this crack in the desired direction. To produce a crack, a scratch must be made with the file, and to this scratch a pointed bit of red-hot charcoal, or the jet of flame produced by the mouth blowpipe, or a very fine gas-flame, or a red-hot glass-rod may be applied. If the heat does not produce a crack, a wet stick or file may be touched upon the hot spot. Upon any part of a glass surface except the edge, it is not possible to control perfectly the direction and extent of this first crack ; at an edge a small crack may be started with tolerable certainty by carrying the file-mark entirely *over* the edge. To guide the crack thus started, a pointed bit of charcoal or slow-match may be used. The hot point must be kept on the glass from 1 c. m. to 0.5 c. m. in advance of the point of the crack. The crack will follow the hot point, and may therefore be carried in any desired direction. By turning and blowing upon the coal or slow-match, the point may be kept sufficiently hot. Whenever the place of experiment is supplied with common illuminating gas, a very small jet of burning gas may be advantageously substituted for the hot coal or slow match. To obtain such a sharp jet, a piece of hard glass tube, No. 5, 10 c. m. long, and drawn to a very fine point (see Ap-

pendix, § 3), should be placed in the caoutchouc tube which ordinarily delivers the gas to the gas-lamp, and the gas should be lighted at the fine extremity. The burning jet should have a fine point, and should not exceed 1.5 c. m. in length. By a judicious use of these simple tools, broken tubes, beakers, flasks, retorts and bottles may often be made to yield very useful articles of apparatus. No sharp edges should be allowed to remain upon glass apparatus. The durability of the apparatus itself, and of the corks and caoutchouc stoppers and tubing used with it, will be much greater, if all sharp edges are removed with the file, or, still better, rounded in the lamp.

3. Bending and Closing Glass-tubes. — Tubing of sizes 5 to 8 inclusive can generally be worked in the common gas- or spirit-lamp ; for larger tubes the blast-lamp is necessary (see Appendix, § 6). Glass tubing must not be introduced suddenly into the hottest part of the flame, lest it crack. Neither should a hot tube be taken from the flame and laid at once upon a cold surface. Gradual heating and gradual cooling are alike necessary, and are the more essential the thicker the glass ; very thin glass will sometimes bear the most sudden changes of temperature, but thick glass and glass of uneven thickness absolutely require slow heating and annealing. When the end of a tube is to be heated, as in rounding sharp edges, more care is required in consequence of the great facility with which cracks start at an edge. A tube should, therefore, always be brought first into the current of hot air beyond the actual flame of the gas- or spirit-lamp, and there thoroughly warmed, before it is introduced into the flame itself. If a blast-lamp is employed, the tube may be warmed in the smoky flame, before the blast is turned on, and may subsequently be annealed in the same manner ; the deposited soot will be burnt off in the first instance, and in the last, may be wiped off when the tube is cold. In heating a tube, whether for bending, drawing or closing, the tube must be *constantly* turned between the fingers, and also moved a little to the right and left, in order that it may be uniformly heated all around, and that the temperature of the neighboring parts may be duly raised. If a tube, or rod, is to be heated at any part but an end, it should be held between the thumb and first two fingers of each hand in such a manner that the hands shall be below the tube, or rod, with the palms upward, while the lamp-flame is between the hands. When the end of a tube, or rod, is to be heated it is best to begin by warming the tube, or rod, about 2 c. m. from the end, and from thence to proceed slowly to the end.

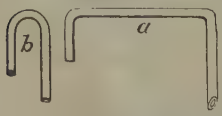
The best glass will not be blackened or discolored during heating. The blackening occurs in glass which, like ordinary flint glass, contains lead (silicate). Glass containing much lead is not well adapted for chemical uses. The blackening may sometimes be removed by putting the glass in the upper or outer part of the flame, where the reducing gases are consumed, and the air has the best access to the glass. The blackening may be altogether avoided by always keeping the glass in the oxidizing part of the flame.

Glass begins to soften and bend below a visible red heat. The condition of the glass is judged of as much by the fingers as the eye ; the hands feel the yielding of the glass, either to bending, pushing or pulling, better than the eye can see the change of color or form. It may be bent as soon as it yields in the hands, but can be drawn out only when much hotter than this. Glass-tubing, however, should not be bent at too low a temperature ; the curves made at too low a heat are apt to be flattened, of unequal thickness on the convex and concave sides, and brittle.

In bending tubing to make gas delivery-tubes and the like, attention should be paid to the following points : 1st, the glass should be equally hot on all sides ; 2d, it should not be twisted, pulled out or pushed together during the heating ; 3d, the bore of the tube at the bend should be kept round, and not altered in size ; 4th, if two or more bends be made in the same piece of tubing (Fig. III, *a*), they should all be in the same plane, so that the finished tube will lie flat upon the level table.

When a tube or rod is to be bent or drawn close to its extremity, a temporary handle may be attached to it by softening the end of the tube, or rod, and pressing against the soft glass a fragment of glass tube, which will adhere strongly to the softened end. The handle may subsequently be removed by a slight blow, or by the aid of a file. If a considerable bend is to be made, so that the angle between the arms will be very small or nothing, as in a siphon, for example, the curvature can not be well produced at one place in the tube, but should be made by heating, progressively, several centimetres of the tube, and bending continuously from one end of the heated portion to the other (Fig. III, *b*). Small and thick tube may be bent more sharply than large or thin tube.

FIG. III.

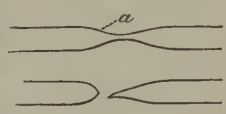


In order to draw a glass tube down to a finer bore, it is simply necessary to thoroughly soften on all sides one or two centimetres'

length of the tube, and then, taking the glass from the flame, to pull the parts asunder by a cautious movement of the hands. The larger the heated portion of glass, the longer will be the tube thus formed. Its length and fineness also increase with the rapidity of motion of the hands. If it is desirable that the finer tube should have thicker walls in proportion to its bore than the original tube, it is only necessary to keep the heated portion soft for two or three minutes before drawing out the tube, pressing the parts slightly together the while. By this process the glass will be thickened at the hot ring.

To obtain a tube closed at one end, it is best to take a piece of tubing, open at both ends, and long enough to make two closed tubes. In the middle of the tube a ring of glass, as narrow as possible, must be made thoroughly soft. The hands are then separated a little, to cause a contraction in diameter at the hot and soft part. The point of the flame must now be directed, not upon the narrowest part of the tube, but upon what is to be the bottom of the closed tube. This point is indicated by the line *a* in Fig. IV. By withdrawing the right hand, the narrow part of the tube is attenuated, and finally melted off, leaving both halves of the original tube closed at one end, but not of the same form; the right-hand half is drawn out into a long point, the other is more roundly closed. It is not possible to close handsomely the two pieces at once. The tube is seldom perfectly finished by the operation; a superfluous knob of glass generally remains upon the end. If small, it may be got rid of by heating the whole end of the tube, and blowing moderately with the mouth into the open end. The knob being hotter, and therefore softer than any other part, yields to the pressure from within, spreads out and disappears. If the knob is large, it may be drawn off by sticking to it a fragment of tube, and then softening the glass above the junction. The same process may be applied to the too pointed end of the right-hand half of the original tube, or to any misshapen result of an unsuccessful attempt to close a tube, or to any bit of tube which is too short to make two closed tubes. When the closed end of a tube is too thin, it may be strengthened by keeping the whole end at a red heat for two or three minutes, turning the tube constantly between the fingers. It may be said in general of all the preceding operations before the lamp, that *success depends on keeping the tube to be heated in constant*

FIG. IV.

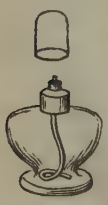


rotation, in order to secure a uniform temperature on all sides of the tube.

4. Blowing Bulbs and Piercing Holes in Tubing. — If the bulb desired is large in proportion to the size of the tube on which it is to be made, the walls of the tube must be thickened by rotation in the flame of the Bunsen burner, or of the blast-lamp, before the bulb can be blown. If the bulb is to be blown in the middle of a piece of tubing, this thickening is effected by gently pressing the ends of the tube together while the glass is red-hot in the place where the bulb is to be ; if the bulb is to be placed at the end of a tube, this end is first closed, and then suitably thickened by keeping the closed end of the tube in the flame, and turning it continually, until enough has been accumulated at the end. The glass is then suddenly withdrawn from the flame, and the thickened portion expanded while hot by steadily blowing, or rather pressing, air into the tube with the mouth ; the tube must be constantly turned on its axis, not only while in the flame, but also while the bulb is being blown. If too strong or too sudden a pressure be exerted with the mouth, the bulb will be extremely thin and quite useless. By watching the expanding glass, the proper moment for arresting the pressure may usually be determined. If the bulb obtained be not large enough, it may be reheated and enlarged by blowing into it again, provided that a sufficient thickness of glass remain.

It is sometimes necessary to make a hole in the side of a tube or other thin glass apparatus. This may be done by directing a pointed flame from the blast-lamp upon the place where the hole is to be, until a small spot is red-hot, and then blowing forcibly into one end of the tube while the other end is closed by the finger ; at the hot spot the glass is blown out into a thin bubble, which bursts, or may be easily broken off, leaving an aperture in the side of the tube.

FIG. V.

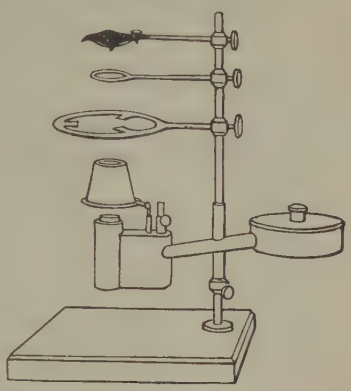


It is hoped that these few directions will enable the attentive student to perform, sufficiently well, all the manipulations with glass tubes which ordinary chemical experiments require. Much practice will alone give a perfect mastery of the details of glass-blowing.

5. Lamps. — The common glass spirit-lamp will be understood without description from the figure (Fig. V). This lamp does not give heat enough for most ignitions ; for such purposes a lamp with circular wick, of some one of the numerous forms sold under the name of Berzelius's Argand

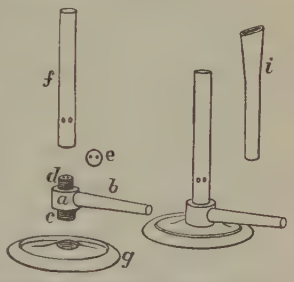
Spirit-Lamp (Fig. VI), is necessary. These argand lamps are usually mounted on a lamp-stand provided with three brass rings, but the fittings of these lamps are all made slender, in order not to carry off too much heat. When it is necessary to heat heavy vessels, other supports must be used.

Fig. VI.



Whenever gas can be obtained, gas-lamps are greatly to be preferred to the best spirit-lamps. For all ordinary experiments, except those for which ignition-tubes must be prepared, or in which considerable lengths of tubing must be heated, the gas-lamp known as Bunsen's burner will be sufficient. Fig. VII represents a cheap and excellent form of the Bunsen lamp. The single casting of brass *a b* comprises the tube *b* through which the gas enters, and the block *a* from which the gas escapes by two or three fine vertical holes passing through the screw *d*, and issuing from the upper face of *d*, as shown at *e*. The length of the tube *b* is 4.5 c. m., and its outside diameter varies from 0.5 c. m. at the outer end to 1 c. m. at the junction with the block *a*. The outside diameter of the block *a* is 1.6 c. m., and its outside height without the screws is 1.8 c. m. By the screw *c*, the piece *a b* is attached to the iron foot *g*, which may be 6 c. m. in diameter. By the screw *d*, the brass tube *f* is attached to the casting *a b*. The diameter of the face *e*, and therefore the internal diameter of the tube *f* should be 8 m. m. The length of the tube *f* is 9 c. m. Through the wall of this tube, four holes 5 m. m. in diameter are to be cut at such a height that the bottom of each hole will come 1 m. m. above the face *e* when the tube is screwed upon *a b*. These holes are of course opposite each other in pairs. The finished lamp is also shown in Fig. VII. To the tube *b* a caoutchouc tube of 5 to

Fig. VII.



7 m. m. internal diameter is attached; this flexible tube should be about 1 m. long, and its other extremity should be connected with the gas-cock through the intervention of a short piece of brass gas-pipe screwed into the cock. In cases where a very small flame is required, as, for instance, in evaporating small quantities of liquid, a piece of wire gauze, somewhat larger than the opening of the tube *f* should be laid across the top of the tube, and its projecting edges pressed down tightly against the sides of the tube before the gas is lighted. In default of this precaution, the flame of a Bunsen burner, when small, and exposed to currents of air, is liable to pass down the tube and ignite the gas at *d*.

A smaller and somewhat cheaper lamp, made on the same principle as the ordinary Bunsen burner, is represented in Fig. VIII. The "tip" of the burner is cast of brass, and the construction will be evident from the enlarged section (*b*). The stand or foot is the same as shown in Fig. VII, except that the opening for the gas is larger. These lamps are excellent where a small flame is required, as it is almost impossible for the gas to "back down" and ignite at the lower opening. Tips are also made, as shown at *c*, the upper opening being closed, and the gas issuing from smaller openings in the sides of the tube forms a "rose"; this form of burner is of especial service when evaporating a solution in a porcelain dish where it is desirable to heat the liquid equably. Either of the tips described may be screwed upon an ordinary gas-burner in default of the stand or foot above represented.

FIG. VIII.

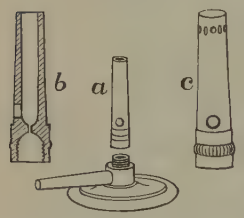
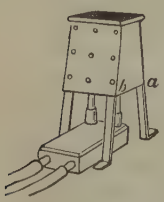


FIG. IX.



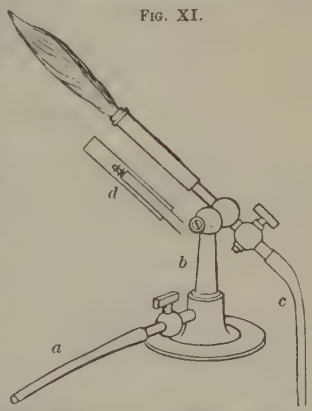
A lamp to give a powerful flame 8 or 10 c. m. long, suitable for heating tubes, may be very simply constructed by boring two holes, entering the side and issuing at the upper face, through a block of compact hard wood, 10 c. m. by 6.5 c. m. by 3.5 c. m., and fitting short pieces of brass tubing into the holes so formed. To the tubes at the side are attached the caoutchouc tubes which deliver the gas, and from the tubes at the top the gas issues under a sheet-iron funnel closed at the top with wire-gauze. Above this gauze, the mixture of gas and air is to be lighted. The

iron funnel will be readily understood from Fig. IX, and the following dimensions ; length of the wire-gauze, 10 c. m ; width of the gauze 5 c. m. ; width at *a b*, 9 c. m. ; height of the line *a b* from the table, 8.5 c. m. ; whole height of the funnel, 21 c. m. A partition parallel to *a b* divides the funnel into two equal parts from the gauze to the level of *a b*. A long flame may also be produced with a Bunsen burner, which may conveniently be somewhat larger than the one described on the preceding page, and which is provided with a copper or brass attachment as represented in Fig. X. This attachment slips over the top of the tube, *f* (see Fig. VII) ; the flame is of the same character as that ordinarily produced, but of a different shape. Two of these lamps side by side will heat a sufficient length of glass or iron tube for all ordinary experiments.

Fig. X.

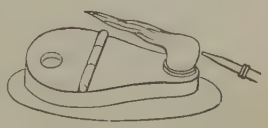
6. Blast-lamps and Blowers. — For drawing, bending and closing large glass tubes, a blast-lamp is necessary. The best form is that sold under the name of Bunsen's Gas Blowpipe. Its construction and the method of using it may be learned from Fig. XI ; *a b* is the pipe through which the gas enters, *c* is the tube for the blast of air ; the relation of the air-tube to the external gas-tube is shown at *d ;* there is an outer sliding tube by which the form and volume of the flame can be regulated.

Fig. XI.



If gas is not to be had, a lamp burning oil or naphtha must be employed. Fig. XII represents a glass-blower's lamp made of tin and suitable for burning oil. A large wick is essential, whether oil or naphtha be the combustible.

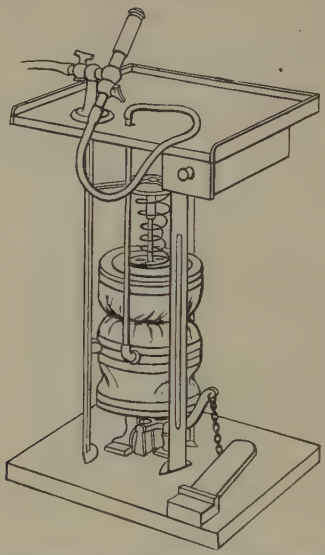
Fig. XII.



For every blast-lamp a blowing-machine of some sort is necessary. To supply a constant blast it is essential that the bellows be of that

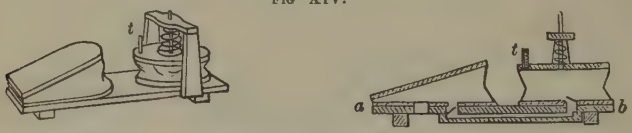
construction called double. Fig. XIII represents a very good form of blowpipe-table, made by J. H. Call, North Billerica, Mass., and

Fig. XIII.



costing about thirty dollars. The bellows are made of seamless rubber cloth ; the table is 0.8 metre high, from which the other dimensions may be inferred. A simpler form of bellows, and one which

Fig XIV.

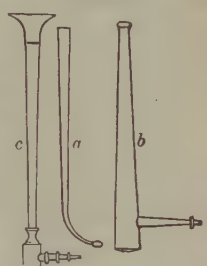


can be made by any carpenter or cabinet-maker, is represented in perspective and in section on Fig. XIV. The sides of the bellows and of the reservoir are made of stout leather. The arrangement of valves will be evident from the figure ; a constant pressure is maintained on the reservoir by means of a spiral spring, and the air is delivered through the tube *t*. The rod which is represented in the figure serves simply as a guide. The entire length from *a* to *b* may be 0.6 metre.

7. Blowpipes. — The mouth-blowpipe in its simplest form is a

tube bent near one extremity at a right angle. Fig. XV, *a*, represents a common form of blowpipe used by jewellers. The blowpipe is rendered more convenient by the addition of a mouth-piece and a chamber near the right angle for the condensation of moisture. Fig. XV, *b* and *c*, represent different forms of blowpipe thus furnished. The cheapest and best form of mouth blowpipe for chemical purposes is a tube of tin-plate, about 18 c. m. long, 2 c. m. broad at one end, and tapering to 0.7 c. m. at the other (Fig. XV, *b*); the broad end is closed, and serves to retain the moisture; a little above this closed end a small cylindrical tube of brass about 5 c. m. long is soldered in at right angles; this brass tube is slightly conical at the end, and carries a small nozzle or tip, which may be made either of brass or platinum. The tip should be drilled out of a solid piece of metal, and should not be fastened upon the brass tube with a screw. A trumpet-shaped mouth-piece of horn or boxwood is a convenient, though by no means essential, addition to this blowpipe. For convenience in cleaning and packing, blowpipes are often made in several pieces, as is the one represented in Fig. XV, *c*.

Fig. XV.



The blowpipe may be used with a candle, with gas or with any hand-lamp proper for burning oil, petroleum or any of the so-called *burning fluids*, provided that the form of the lamp below the wick-holder is such as to permit the close approach of the object to be heated to the side of the wick. When a lamp is used, a wick about 1.2 c. m. long and 0.5 c. m. broad is more convenient than a round or narrow wick. The wick-holder should be filed off on its longer dimension a little obliquely, and the wick cut parallel to the holder, in order that the blowpipe flame may be directed downwards when necessary (Figs. 47, 48, page 130). A gas flame suitable for the blowpipe is readily obtained by slipping a narrow brass tube (*i*), open at both ends, into the tube *f* of Bunsen's burner. (See Fig. VII.) This blowpipe-tube must be long enough to close the air apertures in the tube *f*, and should be pinched together and filed off obliquely on top; it may usually be obtained with the burner from dealers in chemical ware.

8. Caoutchouc. — Vulcanized caoutchouc is a most useful substance in the laboratory, on account of its elasticity, and because it

resists so well most of the corrosive substances with which the chemist deals. It is used in tubing of various diameters comparable with the sizes of glass tubing, and in stoppers of various sizes to replace corks. Caoutchouc tubing may be used to conduct all gases and liquids which do not corrode its substance, provided that the pressure under which the gas or liquid flows be not greater, or their temperature higher, than the texture of the tubing can endure. The flexibility of the tubing is a very obvious advantage in a great variety of cases. Short pieces of such tubing, a few centimetres in length, are much used, under the name of connectors, to make flexible joints in apparatus, of which glass tubing forms part ; flexible joints add greatly to the durability of such apparatus, because long glass tubes bent at several angles and connected with heavy objects, like globes, bottles or flasks full of liquid, are almost certain to break even with the most careful usage ; gas-delivery tubes, and all considerable lengths of glass tubing, should invariably be divided at one or more places, and the pieces joined again with caoutchouc connectors. The ends of glass tubing to be thus connected should be squarely cut, and then rounded in the lamp, in order that no sharp edges may cut the caoutchouc ; the internal diameter of the caoutchouc tube must be a little smaller than the external diameter of the glass tubes ; the slipping on of the connector is facilitated by wetting the glass.

Caoutchouc stoppers of good quality are much more durable than corks, and are in every respect to be preferred. The German stoppers are of excellent shape and quality ; the American, being chiefly intended for wine-bottles, are apt to be too conical. Caoutchouc stoppers can be bored, like corks (see the next section), by means of suitable cutters, and glass tubes can be fitted into the holes thus made with a tightness unattainable with corks. German stoppers may be bought already provided with one, two and three holes. It is not well to lay in a large stock of caoutchouc stoppers, for, though they last a long time when in constant use, they not infrequently deteriorate when kept in store, becoming hard and somewhat brittle with age.

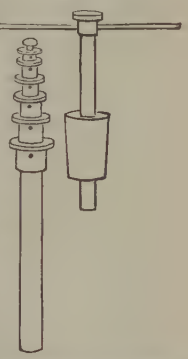
9. Corks. — It is often very difficult to obtain sound, elastic corks of fine grain and of size suitable for large flasks and wide-mouthed bottles. On this account, bottles with mouths not too large to be closed with a cork cut across the grain should be chosen for chemical uses, in preference to bottles which require large corks or bungs cut with the grain, and therefore offering continuous channels for the

passage of gases, or even liquids. The kinds sold as champagne corks and as satin corks for phials are suitable for chemical use. The best corks generally need to be softened before using; this softening may be effected by rolling the cork under a board upon the table, or under the foot upon the clean floor, or by gently squeezing it on all sides with the well-known tool expressly adapted for this purpose, and thence called a cork-squeezer. Steaming also softens the hardest corks.

Corks must often be cut with cleanness and precision; a sharp, thin knife, such as shoemakers use, is desirable for this purpose. When a cork has been pared down to reduce its diameter, a flat file may be employed in finishing; the file must be fine enough to leave a smooth surface upon the cork; in filing a cork, a cylindrical, not a conical form should be aimed at.

In boring holes through corks to receive glass tubes, a hollow cylinder of sheet brass sharpened at one end is a very convenient tool. Fig. XVI. represents a set of such little cylinders of graduated sizes, slipping one within the other into a very compact form; a stout wire, of the same length as the cylinders, accompanies the set, and serves a double purpose, — passed transversely through two holes in the cap which terminates each cylinder, it gives the hand a better grasp of the tool while penetrating the cork; and when the hole is made, the wire thrust through an opening in the top of the cap expels the little cylinder of cork, which else would remain in the cutting cylinder of brass. That cutter whose diameter is next below that of the glass tube to be inserted in the cork is always to be selected, and if the hole it makes is too small, a round file must be used to enlarge the aperture.

FIG. XVI.



Cutters which have been dulled by use may be sharpened by filing or grinding down their outer bevelled edges, and then paring off with a sharp penknife any protuberance or roughness which may remain upon the inside of the edge.

A flask which presents sharp or rough edges at the mouth can seldom be tightly corked, for the cork cannot be introduced into the neck without being cut or roughened; such sharp edges must be rounded in the lamp. In thrusting glass tubes through bored corks,

the following directions are to be observed : (1.) The end of the tube must not present a sharp edge capable of cutting the cork. (2.) The tube should be grasped very close to the cork, in order to escape cutting the hand which holds the cork, should the tube break ; by observing this precaution the chief cause of breakage, viz., irregular lateral pressure, will be at the same time avoided. (3.) A funnel-tube must never be held by the funnel in driving it through a cork, nor a bent tube grasped at the bend, unless the bend comes immediately above the cork. (4.) If the tube goes very hard through the cork, the application of a little soap and water will facilitate its passage, but if soap is used the tube can seldom be withdrawn from the cork after the latter has become dry. (5.) The tube must not be pushed straight into the cork, but screwed in, as it were, with a slow rotary as well as onward motion. Joints made with corks should always be tested before the apparatus is used by blowing into the apparatus and at the same time stopping up all legitimate outlets. Any leakage is revealed by the disappearance of the pressure created. To the same end, air may be sucked out of an apparatus and its tightness proved by the permanence of the partial vacuum. To attempt to use a leaky cork is generally to waste time and labor and to insure the failure of the experiment.

10. Iron-stand, Sand-bath and Wire-gauze. — To support vessels over the gas-lamp, an iron stand is used consisting of a stout vertical rod fastened into a heavy, cast-iron foot, and two or more iron rings of graduated sizes secured to the vertical rod with binding screws ; all the rings may be slipped off the rod, or any ring may be adjusted at any convenient elevation. As a general rule, it is not best to apply the direct flame of the lamp to glass and porcelain vessels ; hence a piece of wire-gauze is stretched loosely over the largest ring, and bent downwards a little for the reception of round-bottomed vessels ; on this gauze, flasks, retorts and porcelain dishes are usually supported. In a few cases, in which a very gradual and equable heat is required, the wire-gauze is replaced by a small, shallow pan, beaten out of sheet-iron, and filled with dry sand. This arrangement is called a sand-bath. With the aid of annealed iron wire, the iron-stand may be made available for supporting tubes over the lamp. Crucibles, or dishes, too small for the smallest ring belonging to the stand, are con-

FIG. XVII.

veniently supported on an equilateral triangle made of three pieces of soft iron wire twisted together at the apices ; this triangle is laid on one of the rings of the stand. An iron tripod — that is, a stout ring supported on three legs — may often be used instead of the stand above described, but it is not so generally useful because of the difficulty of adjusting it at various heights ; with a sufficiency of wooden blocks wherewith to raise the lamp or the tripod as occasion may require, it may be made available.

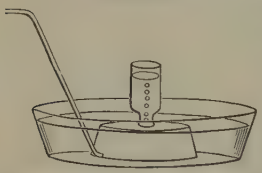
Fig. XVIII.

11. Pneumatic Trough — The pneumatic trough is a contrivance which enables us to collect and confine gases in suitable vessels, and to decant them from one vessel to another. Its efficiency depends on the pressure of the atmosphere, which as we know is capable of supporting a column of water 10.33 metres long or a column of mercury 76 c. m. long, provided that the liquid column be so arranged that the atmospheric pressure shall be fully felt upon the foot of the column, but not at all upon its head. If a tube, closed at one end and open at the other, and of any length less than 10.33 m., be completely filled with water, and then inverted so that its open end shall dip beneath some water held in a basin or saucer, the tube will remain full of water when the thumb or cork, which closed the open end while the inversion was effected, is withdrawn. What is true of a tube is equally true of a bell, or other vessel closed at one end, of any diameter or shape, provided its height be not greater than 10.33 m. ; and the principle which applies to water is equally applicable to mercury, except that the height of the mercury column, which the average atmospheric pressure can hold up, is only 76 c. m., because mercury is 13.596 times heavier than water. If a few bubbles of any gas insoluble in water should be delivered beneath the open end of a tube thus standing full of water in apparent defiance of gravitation, the gas would rise to the top of the tube, by virtue of being lighter than the water, and the exact volume of water displaced by the gas, small or large, would drop into the basin or saucer, beneath. If the gas were thus delivered continuously beneath the tube or bell, we should finally get the tube full of gas, without admixture of air, and sealed at the bottom by the water in the basin or saucer. If mercury were the liquid, the operation would be precisely the same, except as regards the height of the tube. Even this difference of possible height is not noticeable in practice, because bell-glasses and bottles more than

50 c. m. high are very seldom used with either liquid. On account of its costliness, mercury is rarely used, unless the gas to be collected, or experimented upon, be soluble in water. A trough for mercury is made as small as possible for the same reason. It is obvious that the object of a pneumatic trough may be accomplished under a great variety of forms. Any bucket, or tub, with a hanging shelf in it, may be made to serve. It will be sufficient to describe two convenient forms of the apparatus.

A cheap pneumatic trough is represented in Fig. XIX. It consists of two pieces, 1st, a stone-ware pan, about 30 c. m. in diameter on the bottom, with sides sloping slightly outwards and rising to the height of about 10 c. m.; 2d, a deep flower-pot saucer about 15 c. m. in diameter, with one hole bored through the middle of the bottom, and a second arched hole nipped out of its rim; this saucer is inverted in the pan. If this second piece be made expressly for this purpose, it should be made about 5 c. m. high, and its interior should be rounded to the hole in the centre, while the outside is left flat, like the flower-pot saucer. Two blocks of wood of equal thickness, loaded with lead, or two small blocks of stone, may be used instead of the saucer; the delivery-tube rests between them, and the bottle or gas-cylinder is supported directly over the mouth of the delivery-tube. To use this apparatus, the pan is filled with water to a level about 2 c. m. above the top of the inverted saucer; the bottle, cylinder or bell which is to receive the gas is completely filled with water from a pitcher or water-cock, then closed with the hand of the operator, or with a flat piece of glass or wood, inverted into the pan, and placed on the saucer over the hole in its centre; the end of the gas-delivery-tube is thrust through the side hole in the saucer, and the gas rising through the centre hole bubbles up into the bottle or cylinder placed to receive it. While one bottle is filling with gas, another is made ready to replace it, and when the first is full, it is pushed off the centre hole of the saucer, and the second bottle is brought over the hole. A bottle full of gas may be removed from the trough by slipping beneath the mouth of the bottle a shallow plate or dish, and then lifting plate and bottle out of the pan together in such a manner that water enough to seal the mouth of the bottle shall remain in the plate. The gas in one bottle may be decanted upwards into another, by filling

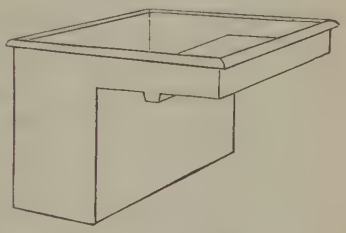
FIG. XIX.



the second bottle with water, and then carefully inclining the bottle containing the gas so as to bring its mouth under the mouth of the bottle which is full of water, keeping the mouths of both bottles all the time beneath the surface of the water in the pan. If the gas which has been collected is heavier than air, a bottle of it may be withdrawn from the water-pan and got at for use, by simply slipping a flat piece of glass or wood beneath its mouth so as to close it rather tightly, and then standing the bottle, mouth upward, upon the table. If the cover be then removed from the bottle, the gas will not flow out, though it will slowly diffuse into the air. As the water with which the bottles or cylinders are filled falls into the pan when displaced by gas, it is possible that the pan may become inconveniently full if many large bottles are used ; this difficulty must be remedied by dipping water out of the pan, and so restoring the true level.

Where considerable quantities of gas are frequently to be handled, and large vessels are therefore necessary, the apparatus shown in Fig. XX is much more convenient than the small pan, which suffices for all common experiments. The form of this larger pneumatic trough, and the mode of using it, will readily be understood from the figure ; the depth and width of the tank or well must be determined by the size of the bells and cylinders which are to be sunk in it, and the length and breadth of the shallow part or shelf by the number of bells or jars of gas which are likely to be in use at any one time. The deep groove in the shelf permits a glass or caoutchouc tube to pass without compression under a bell whose rim projects over the groove. Such a trough is best made of wood lined with lead ; zinc may be used for the lining where no acids are likely to be present. It is very convenient to have it sunk in a table, and permanently provided with a water-cock and drain-pipe. A chief merit of this instrument is that the glass vessels used can be filled with water by sinking them in the well much more conveniently than from a pitcher or water-cock.

FIG. XX.



A pneumatic trough for mercury may be made either of wood, iron or stone. For all common uses, it is very well cut out of a solid block of compact hard wood, which will not split. Small cylinders or bells

only can be used, and the well of the trough should be scooped out but a little larger than the bell or cylinder selected, with its principal dimension horizontal, and its bottom carved to fit the cylindrical bell which is to be laid in it; the shelf, too, should have but a small area, sufficient only for four or five bells of 3 or 4 c. m. diameter.

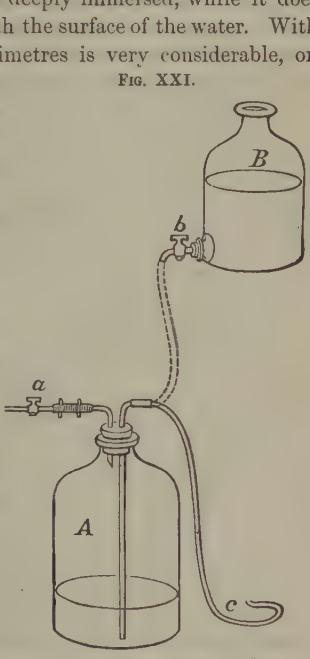
In using a pneumatic trough, of any construction or dimensions, the student should be on his guard against two difficulties of possible occurrence, — against the *sucking back* of the liquid in the trough into the gas-generating apparatus, and against the leakage sometimes induced by the pressure created by thrusting the gas-delivery-tube deep under water or mercury. The first of these difficulties is the most serious. When the flow of gas from a heated flask or tube is suddenly arrested, in consequence of some reduction of temperature, or from any other cause, it often happens that the volume of gas in the generating apparatus contracts, and the cold water or mercury from the trough rises in the delivery-tube to fill the void; if the contraction is so considerable as to suffer the cold liquid to penetrate into the hot flask or tube, an explosion almost inevitably ensues, which fractures the apparatus, if it does no worse damage In collecting over water a gas somewhat soluble in that liquid, this danger is especially imminent. The occurrence of such accidents may be effectually guarded against by paying attention to the following directions: (1.) Whenever it is proposed to stop an evolution of gas which has been going on from a hot flask or tube, withdraw the delivery-tube from the water *before* extinguishing the lamp, and shake off from the bent end of the tube the drops of water which are apt to adhere to it; the lamp may then be safely put out, for air can enter the apparatus through the open tube. (2.) When the flow of gas from a hot apparatus is observed to slacken, watch closely the escape of the gas from the delivery-tube, and as soon as any tendency to reflux of water is detected, lift the delivery-tube quickly out of the water, or, better, slip off the caoutchouc connector, which should always be found between the flask and the water-pan on every such piece of apparatus; if there be no connector, the cork must be loosened in the neck of the flask. Air will thus be admitted to the hot flask or tube.

These precautions apply more particularly to the cases where gas is evolved from dry materials, as in making oxygen or nitrous oxide; when a liquid is contained in the generating flask, a safety-tube (see Fig. 20) is a sure protection against the danger of sucking back. The atmospheric pressure can force air into a flask, in which a partial

vacuum has been created, through the safety-tube, by lifting and displacing a column of the liquid whose height is the length of that portion of the safety-tube which dips beneath the liquid. Unless the liquid in the flask be extraordinarily dense, the force required to do this will be very much less than that required to lift a column of water whose height is determined by the elevation of the highest point of the delivery-tube above the level of the water in the pan.

When the gas coming from the generating flask has to force out and keep out of the delivery-tube a column of water measured from the lowest point of the tube to the surface of the water in the pan, a pressure determined by the height of this column is established upon the interior of the flask and upon every joint of the apparatus. Hence an apparatus will sometimes leak, and refuse to deliver gas at the desired point, when its delivery-tube is deeply immersed, while it does not leak if the tube merely dip beneath the surface of the water. With mercury the pressure of a few centimetres is very considerable, on account of the high specific gravity of the fluid, so that this difficulty is more likely to occur with this metal than with water. Tight joints prevent the occurrence of this difficulty. A partial remedy is to dip the delivery-tube as little as possible below the surface of the fluid in the trough.

FIG. XXI.



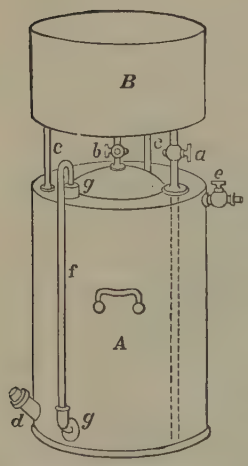
12. Gas-holders. — A small gas-holder, very convenient for many uses, is made from a common glass bottle in the following manner: *A* (Fig. XXI) is a bottle of 4 to 6 litres' capacity; through the cork in its neck pass two glass tubes (No. 6), of which one reaches the bottom of the bottle, while the other merely penetrates the cork; with the outer end of the first tube a caoutchouc tube *c* is connected, with the outer end of the second a common gas-cock *a*. The bottle being first completely filled with water, the apparatus which generates, or contains the gas to be introduced into the holder is connected with the tube carrying the cock *a*; this cock is

open. As the gas presses in, the water mounts in the long tube, and flows out by the siphon *c*. In order to relieve the gas from this pressure at the beginning, it is only necessary to suck a little at *c*. The tube *c* should of course be thrust into a sink or drain-pipe.

To get gas out of the bottle, thus charged, the cock *a* is closed, and the flexible tube *c* is lifted up and connected, as shown in the figure, with a bottle of water *B* placed on a shelf, or stand, somewhat above the bottle *A*. When the cock *b* is opened, the gas in *A* is pressed upon by the weight of the superincumbent column of water, and may therefore be made to issue at will from the cock *a*. The higher *B* is placed above *A*, the greater will be the force with which the gas will issue. If a moderate, or easily regulated water-pressure is at hand, supplied by city water-works or a reservoir in the upper part of the building, the bottle *B* is unnecessary, and the flexible tube *c* may be connected with such a water-supply, whenever gas is to be pressed out of the gas-holder, *A*.

When larger quantities of gas are to be stored for use, a metallic gas-holder, whose construction and proportions are shown in Fig. XXII, is advantageously employed. The open cistern *B* is supported over the vessel *A* on two columns *c*, *c*, and two tubes *a* and *b*; of these tubes, the first, *a*, reaches from the bottom of *B* nearly to the bottom of *A*, while the second, *b*, starts from the bottom of *B* and *just* enters the arched top of *A* without projecting into it; *d* is a short, large tube, sloping upwards and outwards, and capable of being tightly closed with a cork or caoutchouc stopper; *g* is a glass gauge to show the height of the water in the vessel *A*; *e* is the discharge-pipe. To fill the gas-holder with water, close *d*, open the stop-cocks *a*, *b*, and *e*, and pour water into the cistern *B*; the water entering *A* will expel the air through *b* and *e*; when the water begins to flow through *e*, close that stop-cock and expel the rest of the air through *b*. The gas-holder may now be filled with gas by displacing the water in the following manner: — Close all the stop-cocks, withdraw the cork or stopper from *d*, and introduce the tube which

Fig. XXII.



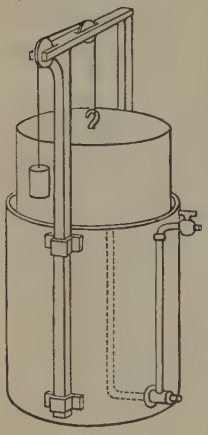
delivers the gas through that opening ; a short piece of caoutchouc tubing makes the best end for the gas-delivery-tube, but glass tubing will answer the purpose if the end be slightly bent upward ; the water flows out at *d* as fast as the gas enters, and the gas-holder should therefore stand in a shallow metal tray provided with a drain-pipe. When the desired quantity of gas has been introduced, close *d*. To draw gas out of a gas-holder of this construction, the cistern *B* is filled with water and the cork *a* is opened ; under the pressure thus established the gas may be drawn off through *e*, or allowed to rise through *b* into bottles or bells filled with water and held over the mouth of the tube *b* in the cistern *B* ; in this last case *B* answers the purpose of a pneumatic trough.

This gas-holder may be cheaply made of zinc ; any gas-fitter can supply the necessary stop-cocks ; care must be taken that the glass tube which constitutes the gauge is fitted air-tight to the gas-holder. The stop-cock *e* need not end in a screw ; tubes may be as well connected with it by caoutchouc. The available pressure, under which the gas in the holder streams out at *e*, is of course limited by the elevation of *B* above *A*, which must always be moderate. When a stronger pressure is desirable, as in getting the oxy-hydrogen blowpipe flame, for example, a heavier water-column may be obtained by screwing a tall tube with a capacious funnel on top of it into the tube *a*, where it opens into the bottom of the cistern *B*. A piece of common iron or copper gas-pipe, about a metre long, answers this purpose very well ; the funnel at the top should hold two or three litres, and must be kept full of water from a cask or tub provided with a cork and placed just above the funnel. Where a water-supply, with moderate pressure, is obtainable, it may be used to keep the funnel full, or to replace the funnel altogether, if directly connected with the tube *a*. A gas-holder, measuring not more than 50 c. m. in total height, is not too heavy to be portable, and during the process of filling may be placed over a tub ; but a gas-holder of much larger proportions is better made a fixture, and provided in a permanent manner with drain-pipe and water-supply. The gas-holder thus described is that which is the most generally useful ; it may be charged from any glass flask, retort or bottle, without any pressure being exerted upon the glass vessel ; and unused gas contained in any sort of bell, bottle, or flask, can be very readily transferred to such a gas-holder without waste and with very little trouble.

A cheaper gas-holder may be made on the plan of the large gas-

holders, improperly called *gasometers*, used in gas-works. Fig. XXIII represents a gas-holder of this sort. Over a tank of water, which may be a cylinder of zinc, as shown in the figure, or a headless pork- or oil-barrel, or any other water-tight tub, is balanced by pulleys and weights a tight bell of zinc, not too large for complete immersion in the tank. The U-tube, shown in the figure, which may be either of lead or brass, serves both to introduce and deliver the gas. To fill such a gasometer, open the cock, lift the counterbalancing weight, and let the bell sink into the water; then connect the vessel from which the gas is delivered with the tube of the holder, counterpoise the bell, and the gas coming from the generator will gradually lift the bell from out the water. To force the gas out of the holder it is only necessary to remove the counterbalancing weight; the weight of the bell forces out the gas, and if this pressure be not sufficient, additional weights may be placed on the top of the bell. Gas-holders of this construction, unless very small, are too heavy, when filled with water, to be carried about; but this difficulty may be obviated, when economy is not specially to be regarded, by placing within the lower cylinder, or tank, a second air-tight cylinder as a core, so as to leave only a narrow space between the inner and outer cylinders for the water into which the upper bell dips. Elegant, but not cheap, gas-holders are thus made, which are convenient for some uses, but are not so generally to be recommended as those of the construction first described. The vessel from which a gas-holder with counterpoised bell is charged is always subjected to some pressure, slight if the pulleys, cords and weights are in perfect order, but more frequently considerable on account of the difficulty of maintaining such an apparatus in perfect condition.

Fig. XXIII.



13. Deflagrating Spoon. — The little cup which holds combustible material, to be burnt in a bottle or jar of gas, is called a deflagrating spoon; it may be cheaply made by hollowing a hemispherical cup out of a cube of chalk about 2 c. m. on a side, and attaching a stout iron or brass wire to the chalk, in such a manner that the cup will be right side up when hung by the wire in a jar

of gas ; the upper end of this wire should be straight, that it may be thrust through the cork or piece of wood which covers the mouth of the bottle or jar. The piece of chalk may be replaced by a bit of the cylindrical crayons commonly used with blackboards. Brass deflagrating spoons are also to be had of philosophical instrument-makers.

14. Platinum Foil and Wire. — A piece of platinum foil about 3 c. m. square is useful in experiments involving the evaporation of a drop or two of a liquid or the heating of a small quantity of a solid substance. The foil should be at least so thick that it does not crinkle when wiped ; and it is more economical to get foil which is too thick than too thin, for it requires frequent cleaning. A bit of platinum-wire, 0.4 m. m. in diameter and 8 c. m. long, will last a long time with careful usage. No other metal, and no mixture of substances from which a metal can be reduced, must ever be heated on platinum-foil or wire, for platinum forms alloys with other metals which are much more fusible than itself. If once alloyed with a baser metal, the platinum ceases to be applicable to its peculiar uses. Platinum may be cleaned by boiling it in either nitric or chlorhydric acid, by fusing the acid sulphate of sodium or potassium upon it, or by scouring it with fine sand. Aqua-regia (§ 75) and chlorine-water dissolve platinum ; the sulphides, cyanides and oxides of sodium and potassium, when fused in platinum vessels, slowly attack the metal.

15. Filtering. — Filtration is resorted to in order to separate a finely divided solid from a liquid. The filter may be made of paper, cloth, tow, cotton, asbestos, and other substances. Paper is the substance oftenest used. A good filtering paper must be porous enough to filter rapidly, and yet sufficiently close in texture to retain the finest powders ; and it must also be strong enough to bear, when wet, the pressure of the liquid which must be poured upon it.

Filtering paper is commonly sold in sheets, which may be cut into circles of any desired diameters for use, according to the various scales of operation and quantities of liquids to be filtered, or packages of "cut-filters" may be procured ready-made from the dealers in chemical ware.

There are two ready methods of preparing filters for use. According to the first method, shown in Fig. XXIV, a circle of paper is folded over on its own diameter, and the semicircle thus obtained is doubled once upon itself into the form of a quadrant ; the paper thus folded is opened so that three thicknesses shall come upon one side,

Fig. XXIV.

and one thickness upon the other, as shown in the upper half of Fig. XXIV ; the filter is then placed in a glass funnel, the angle of which should be precisely that of the opened paper, viz., 60°. The paper may be so folded as to fit a funnel whose angle is more or less than 60°, but this is the most advantageous angle, and funnels should be selected with reference to their correctness in this respect.

In the second method of folding filters, the circle of paper is doubled once upon itself as before into the form of a semicircle, and a fold equal to one quarter of this semicircle is turned down on each side of the paper. Each of the quarter semicircles is then folded back upon itself, as shown in the lower half of Fig. XXV ; the filter is opened, without disturbing the folded portions, and placed in the funnel. Filtration can be rapidly effected with this kind of filter, for the projecting folds keep open passages between the filter and the funnel, and thus facilitate the passage of the liquid. That portion of the circle of paper which must necessarily be folded up in order to give the requisite conical form to a paper filter retards filtration in the first manner of folding, but helps it in the second.

Fig. XXV.

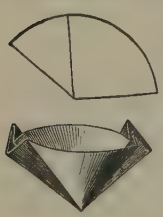


Fig. XXVI.

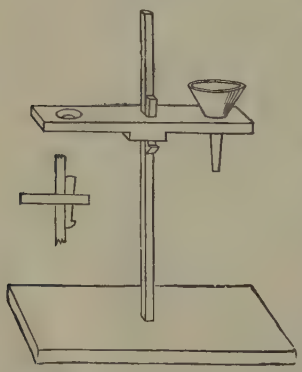


Fig. XXVII.

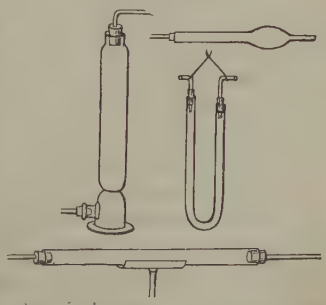
Coarse and rapid filtering can be effected with cloth bags ; also by plugging the neck of a funnel loosely with tow or cotton. If a very acid or very caustic liquid, which would destroy paper, cotton, tow or wool, is to be filtered, th best substances wherewith to plug the neck of the funnel are asbestos and gun-cotton, neither of which is attacked by such corrosive liquids.

The glass funnel which holds the filter generally requires an independent support, for it is seldom judicious, or possible, to support

the funnel directly upon the vessel which receives the *filtrate*, as the clear liquid which runs through the filter is called. The iron stand (Fig. XVII) may be used for this purpose ; and wooden stands, of the form represented in Fig. XXVI, adapted expressly for holding funnels, are very convenient and not expensive. In general, care should be taken that the lower end of the funnel touch the side or edge of the vessel into which the filtrate descends, in order that the liquid may not fall in drops, but run quietly down without splashing. Sometimes there is no objection to thrusting a funnel directly into the neck of a bottle or flask, but in this case an ample exit for the air in the bottle must be provided (Fig. XXVII).

16. Drying Gases. — It is often desirable to remove the aqueous vapor which is mixed with gases collected over water, or prepared from materials containing water. It very seldom happens that a gas can be prepared at one operation in so dry a state as to contain no vapor of water ; this vapor must ordinarily be removed by a subsequent or additional process. Experience has shown that some gases are more easily dried than others ; thus air, hydrogen and common oxygen are thoroughly dried with great ease, but gases which contain antozone only with great difficulty ; chlorine is three times as hard to dry as carbonic acid. These and similar facts must be borne in mind in constructing drying apparatus. The common drying process depends upon bringing the moist gas into contact with some liquid or solid which greedily and rapidly absorbs aqueous vapor. The three substances most used for this purpose are concentrated sulphuric acid, calcium chloride and dry quicklime. Sulphuric acid may be used in two ways : the gas may be made to bubble through a few centimetres' depth of the liquid acid, or it may be forced to pass through the interstices of a column of broken pumice-stone which has been previously soaked in the acid. The latter method is the most effectual, because it secures a more thorough contact of the gas with the hygroscopic acid than is possible during the rapid bubbling of the light gas through a shallow layer of the dense liquid. The column of fragments of pumice-stone may be held in a

Fig. XXVIII.



U-tube, arranged like that shown in Fig. XXVIII ; but the vertical cylinder shown in the same figure is better adapted for this use, because the acid, as it becomes dilute from absorption of moisture, gradually trickles from the pumice-stone, and is apt to collect in such quantity at the bottom of the U-tube as to completely close the tube. In preparing the upright cylinder for use, the portion below the contraction is not filled with pumice-stone ; it receives the drippings from the pumice-stone column. The gas to be dried enters by the lower lateral opening, and goes out at the top of the cylinder. Though especially adapted to the column of acid-soaked pumice-stone, this cylinder may very well be used with either of the other drying agents, calcium chloride or quicklime. Either of the forms of drying-tube represented in Fig. XXVIII may be employed with these latter substances ; in charging the horizontal tubes, bits of loose cotton-wool should first be placed against the exit-tube to prevent any particles of the calcium chloride, or quicklime, from entering that tube ; pieces of the perfectly dry solid are then introduced in such a way that the tube may be compactly filled with fragments which leave room for the gas to pass very deviously between them, but offer no direct channels through which the gas could find straight and quick passage. Quicklime must be charged much more loosely than calcium chloride, because of its great expansion when moistened. Fused calcium chloride is not so well adapted for drying gases as the unfused substance. It is not at all necessary that the fragments of calcium chloride, or quicklime, should be of uniform size. When the tube is nearly full, a plug of loose cotton should be inserted before putting in the cork. A calcium chloride tube, once filled, will often serve for many experiments ; whenever out of use, its outlets should be covered with paper caps ; or, better, caoutchouc connectors may be slipped upon the exit-tubes, and bits of glass rod thrust into these connectors. The moisture of the air is thus kept from the calcium chloride. The dimensions of drying-tubes are of course very various ; the bulb-tube shown in Fig. XXVIII is seldom used with a greater length than 25 c. m. ; when this form of tube is employed the gas should invariably enter by the end without a cork, where the small size of the tube permits direct connection with a common gas-delivery-tube by means of a caoutchouc connector ; the other horizontal tube, shown in the figure, may be of any length, but whenever a great extent of drying surface is necessary, U-tubes have the advantage of compactness, for many can be hung upon one short frame ; the upright cylinder may be from 25 c. m. to 40 c. m. in height.

The choice between one or other of the three drying substances is determined in each special case by the chemical relations of the gas to be dried ; thus ammonia-gas, which is absorbed by sulphuric acid and by calcium chloride, must be dried by passing it over quick-lime, while sulphurous acid gas, which would combine with quick-lime, must be dried by contact with sulphuric acid.

17. Water-bath. — It is often necessary to evaporate solutions at a moderate temperature which can permanently be kept below a certain known limit ; thus, when an aqueous solution is to be quietly evaporated without spirting or jumping, the temperature of the solution must never be suffered to rise above the boiling-point of water, nor even quite to reach this point. This quiet evaporation is best effected by the use of a water-bath, — a copper cup whose top is made of concentric rings of different diameters to adapt it to dishes of various sizes (Fig. XXIX). This cup, two-thirds full of water, is supported on the iron-stand over the lamp, and the dish containing the solution to be evaporated is placed on that one of the several rings which will permit the greater part of the dish to sink into the copper cup. The steam rising from the water impinges upon the bottom of the dish, and brings the liquid within it to a temperature which insures the evaporation of the water, but will not cause any actual ebullition. The water in the copper cup must never be allowed to boil away. Wherever a constant supply of steam is at hand, as in buildings warmed by steam, the copper cup above described may be converted into a steam-bath by attaching it to a steam-pipe by means of a small tube provided with a stop-cock.

Fig. XXIX.

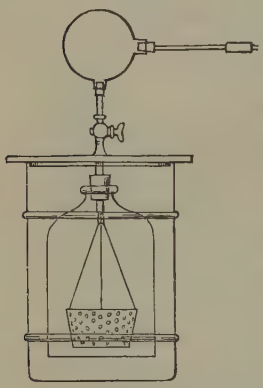
A cheap but serviceable water-bath may be made from a quart milk-can, oil-can, tea-canister, or any similarly shaped tin vessel, by inserting the stem of a glass funnel into the neck of the can through a well-fitting cork. In this funnel the dish containing the liquor to be evaporated rests. The can contains the water, which is to be kept just boiling. On account of the shape of the funnel, dishes of various sizes can be used with the same apparatus.

When a gradual and equable heat higher than can be obtained upon the water-bath is required, a sand-bath will sometimes be found useful. A cheap and convenient sand-bath may be made by beating a disk of thin sheet-iron, about four inches in diameter, into the form of a saucer or shallow pan, and placing within it a quantity of dry

sand. The dish or flask to be heated is embedded in the sand, and the apparatus placed upon a ring of the iron-stand over a gas-lamp.

18. Self-regulating Gas-generator. — An apparatus which is always ready to deliver a constant stream of hydrogen, and yet does not generate the gas, except when it is immediately wanted for use, is a great convenience in an active laboratory or on a lecture-table. The same remark applies to the two gases, hydrogen sulphide and carbonic acid, which are likewise used in considerable quantities, and which can be conveniently generated in precisely the same form of apparatus which is advantageous for hydrogen. Such a generator may be made of divers dimensions. The following directions, with the accompanying figure (Fig. XXX), will enable the student to construct an apparatus of convenient size. Procure a glass cylinder 20 or 25 c. m. in diameter and 30 or 35 c. m. high; ribbed candy-jars are sometimes to be had of about this size; procure also a stout tubulated bell-glass 10 or 12 c. m. wide and 5 or 7 c. m. shorter than the cylinder. Get a basket of sheet-lead 7.5 c. m. deep and 2.5 c. m. narrower than the bell-glass, and bore a number of small holes in the sides and bottom of this basket. Cast a circular plate of lead 7 m. m. thick and of a diameter 4 c. m. larger than that of the glass cylinder; on what is intended for its under side solder three equidistant leaden strips, or a continuous ring of lead, to keep the plate in proper position as a cover for the cylinder. Fit tightly to each end of a good brass gas-cock a piece of brass tube 8 c. m. long, 1.5 to 2 c. m. wide, and stout in metal. Perforate the centre of the leaden plate, so that one of these tubes will snugly pass through the orifice, and secure it by solder, leaving 5 c. m. of the tube projecting below the plate. Attach to the lower end of this tube a stout hook on which to hang the leaden basket. By means of a sound cork and common sealing-wax, or a cement made of oil mixed with red and white lead, fasten this tube into the tubulure of the bell-glass air-tight, and so firmly that the joint will bear a weight of several pounds. Hang the basket by means of copper wire within the bell 5 c. m. above the bottom of the latter. To the tube which extends

Fig. XXX.



above the stop-cock attach by a good cork the neck of a tubulated receiver of 100 or 150 c. c. capacity, the interior of which has been loosely stuffed with cotton. Into the second tubulure of the receiver fit tightly the delivery-tube carrying a caoutchouc connector; into this connector can be fitted a tube adapted to convey the gas in any desired direction. This apparatus is charged by placing the zinc, iron sulphide or marble, as the case may be, in the basket, hanging the basket in the bell, and then putting the bell-glass full of air into its place and closing the stop-cock; the cylinder is then filled with dilute acid to within 4 c. m. of the top. On opening the cock, the weight of the acid expels the air from the bell, the acid comes in contact with the solid in the basket, and a steady supply of gas is generated until either the acid is saturated or the solid dissolved: if the cock be closed, the gas accumulates in the bell, and pushes the acid below the basket, so that all action ceases. In cold weather the apparatus must be kept in a warm place. For generating hydrogen, sulphuric acid diluted with four or five parts of water is used; for hydrogen sulphide, sulphuric acid is diluted with fourteen parts of water; for carbonic acid, chlorhydric acid diluted with two or three parts of water is to be preferred.

19. Glass Retorts, Flasks, Beakers, Test-tubes, Test-glasses and Bottles. — All glass vessels which are meant for use in heating liquids must have uniformly thin bottoms. Tubulated retorts are much more generally useful than those without a tubulure; as retorts are expensive in comparison with flasks, they are less used than formerly.

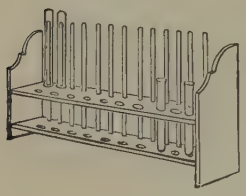
The neck of a flask should have such a form that it can be tightly closed by a cork, and the lip must be strengthened to resist the force used in pressing in the cork, either by a rim of glass added on the outside, or better by causing the rim itself to flare outward. The actual edge of the rim must never be sharp or rough, but always smooth and rounded by partial fusion.

Beakers are thin flat-bottomed tumblers with a slightly flaring rim. They are to be bought in sets or nests which sometimes include a large range of sizes. The small sizes are very useful vessels; the large are so fragile as to be almost worthless. Up to the capacity of about a litre, beakers are to be recommended for heating liquids whenever it is an object to have the whole interior of the vessel readily accessible.

Test-tubes are little cylinders of thin glass, with round, thin bot-

toms, and lips slightly flared. Their length may be from 12 c. m. to 18 c. m., and their diameter 1 c. m. to 2 c. m. ; they should never have a diameter so large that the open end cannot be closed by the ball of the thumb. To hold the tubes upright a wooden rack is necessary ; besides the row of holes to receive a dozen test-tubes bottom down, the rack should have a row of pegs on which the test-tubes may be inverted when not in use ; in this position the water in which they are rinsed drains off, and dust cannot be deposited within the tubes. Test-tubes are much used for heating small quantities of liquid over the gas- or spirit-lamp ; they may generally be held by the upper end in the fingers without inconvenience, but if a liquid is to be boiled long in a test-tube, the tube must be held in wooden nippers (see **Fig. 1**), or in a strip of thick folded paper, nipped round the tube and grasped between the thumb and forefinger just outside the tube. The wooden nippers, above mentioned, are made of two bits of wood about a foot long hinged together at the back, and at once connected and kept apart by a sliding steel or brass spring, somewhat like those used on certain pruning-shears and some kinds of steel nippers. When a liquid is boiling actively in a test-tube, it sometimes happens that portions of the hot liquid are projected out of the tube with some force ; the operator should always be careful not to direct a tube, which he is thus using, either towards himself or towards any other person in his neighborhood. Test-tubes are cleaned by the aid of cylindrical brushes, made of bristles caught between twisted wires, like those used for cleaning lamp-chimneys : they should have a round end of bristles.

Fig. XXXI.



An excellent holder (see **Fig. 35**), devised by Professor Caldwell, is made of flexible copper or brass wire, 1½ m.m. thick. This wire is twisted about a cork which serves as a handle, or, being perforated, the cork may be slipped on to the rod of a ring-stand. By opening the coils at the ends more or less, it can be adapted to any test-tube or ignition tube, and the tube can be supported at any angle.

Two precautions are invariably to be observed in heating test-tubes ; first, the outside of the tube must be wiped perfectly dry ; secondly, the tube must be moved in and out of the flame for a minute or two when first heated. It should be rolled to and fro also to a slight extent between the thumb and forefinger, in order that each side of it

may be equally exposed to the flame. A drop of water on the outside of the tube keeps one spot cooler than the rest. The tube breaks, because its parts, being unequally heated, expand unequally, and tear apart.

In heating glass and porcelain vessels of whatever form, the temperature must not be raised too rapidly. When a large flask or beaker containing a cold liquid is first warmed over a lamp, moisture almost invariably condenses upon the bottom of the vessel : this moisture should be wiped off with a cloth.

Stout conical glasses with strong stems and feet are convenient for many uses not involving the application of heat. They are called test-glasses, and may be had of various shapes and sizes. It is obvious that cheap wine- or beer-glasses and common jelly-tumblers would answer the purposes which these test-glasses serve.

For the collection of gases at the pneumatic trough, and for many other purposes, ordinary green glass "packing-bottles" may take the place of more expensive apparatus. The smaller sizes may be conveniently used instead of beakers and test-glasses, but the bottles cannot be used for the heating of liquids.

20. Pipettes. — Pipettes are tubes drawn to a point and sometimes furnished with a bulb or a cylindrical enlargement. They are chiefly used to suck small quantities of fluid out of a vessel without disturbing the bulk of the liquid. Fig. XXXII represents three forms of pipette ; the form with the lower end bent upwards is used to introduce liquids into a bell or bottle of gas standing over mercury. Pipettes graduated into cubic centimetres, or holding a certain number of cubic centimetres when filled to a mark on the stem, are often convenient.

Fig. XXXII.

Measuring-glasses, divided into cubic centimetres, are made in the cylindrical form and also in the flaring shape common in druggists' measuring-glasses ; the cylindrical form is to be preferred. Such a glass of 250 c. c., or better of 500 c. c. capacity, is a very useful implement : flasks holding 1 litre, 500 c. c., or 250 c. c., when filled to a mark on the neck, are also convenient.

21. Porcelain Dishes and Crucibles. — Open dishes, which will bear heat without cracking, are necessary implements in the laboratory for conducting the evaporation of liquids. The best evaporating-dishes are those made of Berlin porcelain, glazed both inside

and out, and provided with a little lip projecting beyond the rim. The dishes made of Meissen porcelain are not glazed on the outside, and are not so durable as those of Berlin manufacture ; but they are much cheaper, and with proper care last a long time. The small Berlin dishes will generally bear an evaporation to dryness on the wire-gauze over the open flame of the gas-lamp ; the Meissen dishes do not so well endure this severe treatment. Evaporating-dishes are made of all diameters from 3 c. m. to 45 c. m. ; they should be ordered by specifying the diameter desired. The large sizes are expensive, and not very durable ; they should never be used except on a sand-bath. Dishes of German earthenware are as good as porcelain for many uses, and are much to be recommended in place of the large sizes of porcelain dishes.

Fig XXXIII.

Deep porcelain dishes provided with handles (called *casseroles*) are very useful in heating liquids which have a tendency to froth (see **Exps. 111** and **113**), and may be obtained of various sizes.

Very thin, highly glazed porcelain crucibles with glazed covers are made both at Berlin and at Meissen, near Dresden ; they are indispensable implements to the chemist. In general, the Meissen crucibles are thinner than the Berlin, but the Berlin crucibles are somewhat less liable to crack ; both kinds are glazed inside and out, except on the outside of the bottom. Crucibles should be ordered by specifying the diameters of the sizes desired ; they are to be had of nearly a dozen different sizes, with diameters varying from 2 c. m. to 9 c. m. The smallest and largest sizes are little used ; for most purposes the best sizes are those between 3 c. m. and 5 c. m. in diameter. As the covers are much less liable to be broken than the crucibles, it is advantageous to buy more crucibles than covers, whenever it is possible so to do. Porcelain crucibles are supported over the lamp on an iron-wire triangle ; they must always be gradually heated, and never brought suddenly in contact with any cold substance while they are hot.

22. Rings to Support round-bottomed Vessels. — It is often necessary to support globes, round-bottomed flasks, evaporating-dishes, and round receivers in a stable manner upon the table or other flat surface. For this purpose rings are used, made of braided straw, or of straw wound about a core of straw, or of tin wound with listing or coarse woollen cloth. The material of which these rings are made, or with which they are covered, ought to be a substance which

does not conduct heat well, because one of the chief uses of these rings is to receive hot vessels just removed from the lamp or sand-bath. A hot flask or dish would almost certainly be broken, if it were placed upon the cold surface of a good conductor of heat. The student must never touch a hot vessel with cold water, or bring it into sudden contact with a surface of marble, iron, copper, or other good conductor of heat.

23. Crucibles, Furnaces, Tongs and Iron Retort. — For preparing granulated zinc on a considerable scale and for other purposes, the cheapest crucibles, and those which are most used, are those known as Hessian crucibles. These Hessian crucibles are sold in nests containing from 3 to 10 crucibles ; there are 10 sizes, which vary from 3 to 25 c. m. in height. They generally have a triangular form, and will withstand a very high temperature, if they are warmed before being put in the fire. They are not sold with covers ; but covers may be bought separately, or a triangular piece of soapstone may be very conveniently used as a cover. Crucibles are mainly used for the fusion and reduction of metals, but there are also many chemical compounds which can only be prepared at the very high temperatures which by the use of crucibles we are able to command. Although crucibles often withstand the most sudden changes of temperature, it is, nevertheless, expedient as a general rule to heat up a crucible gradually, and to previously warm a charge which is to be placed in a crucible already hot. If a cold crucible is to be introduced into a fire, it should first be placed in the coldest part of the fire and gradually brought into the hottest part.

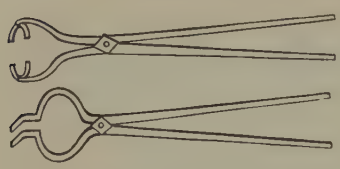
For heating these crucibles an anthracite or coke fire in an ordinary cylinder stove will in most cases suffice. The chafing-dish or open portable stove, such as is used by plumbers, for example, is very convenient for operations which require less heat. The clay buckets used as open furnaces are better than the iron ones, because they hold the heat better.

Charcoal is the fuel used in these open fires. A very useful accompaniment to these portable furnaces is a piece of straight stove-pipe, about 60 c. m. long and 10 c. m. wide, and flaring out below like a funnel until it is wide enough to cover the top of the furnace. This contrivance powerfully increases the draught, and is used to urge the fire during kindling, or to intensify it while a fusion is in progress. With a furnace of this description there is no difficulty in keeping a small crucible white-hot for a short time.

Small porcelain crucibles are handled, when hot, by means of small steel or iron tongs, such as are represented in Fig. XXXIV, or by means of small steel pincers, such as are used by jewellers. Larger crucibles are handled by means of tongs of various shapes and sizes, according to the weight and nature of the vessels to be lifted. Fig. XXXV represents two good forms of stout iron tongs for lifting large crucibles out of a coal fire. The manner of using them is readily understood from the figure.

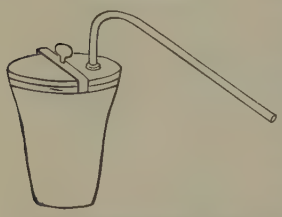
Fig. XXXIV.

Fig. XXXV.



A retort, made of iron, of the form shown in Fig. XXXVI, is a very convenient tool in making large quantities of oxygen, and in preparing illuminating-gas or marsh-gas. The iron top is fitted to the retort with a ground joint fastened by a screw-clamp. When the top is removed, the whole inner surface of the retort is exposed, — a decided advantage wherever the residue left in the retort after use is solid. A retort of about 300 c. c. capacity is amply large for most uses. A small iron kettle makes a serviceable retort ; the lid must be luted on, and the nose becomes the exit-tube.

Fig. XXXVI.



24. Mortars. — Iron, porcelain and agate mortars are used by chemists to reduce solids to powder. An iron mortar is useful for coarse work, and for effecting the first rough breaking up of substances which are subsequently powdered in the porcelain or agate mortar. If there be any risk of fragments being thrown out of the mortar, it should be covered with a cloth or piece of stiff paper, having a hole in the middle through which the pestle may be passed. Pieces of stone, minerals and lumps of brittle metals may be safely broken into fragments suitable for the mortar by wrapping them in strong paper, laying them so enclosed upon an anvil and striking them with a heavy hammer. The paper envelope retains the broken particles, which might otherwise fly about in a dangerous manner, and be lost.

The best porcelain mortars are those known by the name of Wedge-

wood-ware, but there are many cheaper substitutes. Porcelain mortars will not bear sharp and heavy blows ; they are intended rather for grinding and trituration than for hammering ; the pestle may either be formed of one piece of porcelain, or a piece of porcelain cemented to a wooden handle ; the latter is the less desirable form of pestle. Unglazed porcelain mortars are to be preferred. In selecting mortars, the following points should be attended to, — 1st, the mortar should not be porous ; it ought not to absorb strong acids or any colored fluid, even if such liquids be allowed to stand for hours in the mortar ; 2d, it should be very hard, and its pestle should be of the same hardness ; 3d, it should be sound ; 4th, it should have a lip for the convenience of pouring out liquids and fine powders. As a rule, porcelain mortars will not endure sudden changes of temperature. They may be cleaned by rubbing in them a little sand soaked in nitric or sulphuric acid, or, if acids are not appropriate, in caustic soda.

Agate mortars are only intended for trituration ; a blow would break them. They are exceedingly hard, and impermeable. The material is so precious and so hard to work, that agate mortars are always small. The pestles are generally inconveniently short, — a difficulty which may be remedied by fitting the agate pestle into a wooden handle.

In all grinding operations in mortars, whether of porcelain or agate, it is expedient to put only a small quantity of the substance to be powdered into the mortar at once. The operation of powdering will be facilitated by sifting the matter as fast as it is powdered, returning to the mortar the particles which are too large to pass through the sieve.

25. Spatulæ. — For transferring substances in powder, or in small grains or crystals, from one vessel to another, spatulæ and scoops made of horn or bone are convenient tools. A coarse bone paper-knife makes a good spatula for laboratory use. Cards, free from glaze and enamel, are excellent substitutes for spatulæ.

26. Thermometers. — Thermometers intended for chemical use must have no metal, and no wood or other organic material upon their outer surfaces ; their external surfaces must be wholly of glass. The best thermometers are straight glass tubes, of uniform diameter, with cylindrical instead of spherical bulbs, and having the scale engraved upon the glass ; such instruments can be passed tightly through a cork, and are free from many liabilities to error to which thermometers with paper or metal scales are always exposed. A cheaper kind of thermometer, having a paper scale enclosed in a glass envelope, will answer for most experiments.

THE METRICAL SYSTEM OF WEIGHTS AND MEASURES.

The metrical system, employed in the affairs of every-day life by most of the nations of continental Europe and by scientific writers throughout the world, is based upon a fundamental unit, or measure of length, called a *metre*. This metre is defined as the 40-millionth part of the circumference of the earth, or, in other words, of a "great circle" or meridian; its length was originally determined by actual measurement of a considerable arc of a meridian, but the various measurements heretofore made of the length of the earth's meridian differ slightly from each other, and it is to be expected, and indeed hoped, that the steady improvements of methods and instruments will make each successive determination of the length of the meridian better than, and therefore different from, the preceding. It is, on this account, necessary to define the standard of length, by legislation, to be a certain rod of metal, deposited in a certain place under specified guaranties, and to secure the uniformity and permanence of the standard by the multiplication of exact copies in safe places of deposit.

From this single quantity, the metre, all other measures are decimally derived. Multiplied or divided by 10, 100, 1000, and so forth, the metre supplies all needed linear measures, and the square metre and cubic metre, with their decimal multiples, supply all needed measures of area or surface, on the one hand, and of solidity or capacity on the other.

From the unit of measure to the unit of weight the transition is admirably simple and convenient. The cube of the 1-hundredth of the linear metre is, of course, the millionth of the cubic metre; its bulk is about that of a large die of the common backgammon board. This little cube of pure water is the universal unit of weight, a *gramme*, which, decimally multiplied and divided, is made to express all weights. The numbers expressing all weights, from the least to the greatest, find direct expression in the decimal notation; the weights used in different trades only differ from each other in being different decimal multiples of the same fundamental unit; and in comparing together weights and volumes, none but easy decimal computations are ever necessary.

The nomenclature of the metrical system is extremely simple ; one general principle applies to each of the following tables. The Greek prefixes for 10, 100 and 1000, viz., deca, hecto and kilo, are used to signify multiplication, while the Latin prefixes for 10, 100 and 1000, viz., deci, centi and milli, are employed to express subdivision. Of the names thus systematically derived from that of the unit in each table, many are not often used ; the names in common use are those printed in small capitals. Thus in the table for linear measure, only the metre, kilometre, centimetre and millimetre are in common use, — the first for such purposes as the English yard subserves, the second instead of the English mile, the third and fourth in lieu of the fractions of the English foot and inch.

LINEAR MEASURE.

			Metre.
Divisions	MILLIMETRE	=	0.001 or 1-1,000 of a metre.
	CENTIMETRE	=	0.01 or 1-100 "
	Decimetre	=	0.1 or 1-10 "
Unit	METRE	=	1.
Multiples	Decametre	=	10.
	Hectometre	=	100.
	KILOMETRE	=	1,000.

SURFACE MEASURE.

Divisions	Millimetre square	=	0.000,001 of a metre square.
	Centimetre square	=	0.000,1 " "
	Decimetre square	=	0.01 " "
Unit	METRE SQUARE	=	1. " "

CUBIC MEASURE.

			Cubic Metre.
Divisions	Cubic Millimetre	=	0.000,000,001
	Cubic Centimetre	=	0.000,001
	Cubic Decimetre	=	0.001
Unit	CUBIC METRE	=	1.
Multiples	Cubic Decametre	=	1,000.
	Cubic Hectometre	=	1,000,000.
	Cubic Kilometre	=	1,000,000,000.

The table for land measure we omit, as having no connection with our subject. For the measurement of wine, beer, oil, grain and similar wet and dry substances, a smaller unit than the cubic metre is desirable. The cubic decimetre has been selected as a special standard of capacity for the measurement of substances such as are bought and sold by the English wet and dry measures. The cubic decimetre thus used is called a *litre.*

CAPACITY MEASURE.

		Litres.	Cubic Metre.	
Divisions .	Millilitre	= 0.001	= 0.000,001	= 1 cubic centimetre.
	Centilitre	= 0.01	= 0.000,01	
	Decilitre	= 0.1	= 0.000,1	
Unit . .	Litre	= 1.	= 0.001	= 1 cubic decimetre.
Multiples .	Decalitre	= 10.	= 0.01	
	Hectolitre	= 100.	= 0.1	
	Kilolitre	= 1,000.	= 1.	= 1 cubic metre.

The table of weights bears an intimate relation to this table of capacity. As already mentioned, the weight of that die-sized cube, a cubic centimetre or millilitre of distilled water (taken at 4°, its point of greatest density) constitutes the metrical unit of weight. This weight is called a *gramme*. From the very definition of the gramme, and from the table of capacity-measure, it is clear that a litre of distilled water at 4° will weigh 1,000 grammes.

WEIGHTS.

		Grammes.	
Divisions .	Milligramme	= 0.001	
	Centigramme	= 0.01	
	Decigramme	= 0.1	
Unit . .	Gramme	= 1.	= 1 cubic centimetre of water at 4°.
Multiples .	Decagramme	= 10.	
	Hectogramme	= 100.	
	Kilogramme	= 1,000.	= 1 cubic decimetre of water at 4°.

The simplicity and directness of the relations between weights and volumes in the metrical system can now be more fully explained. The chemist ordinarily uses the gramme as his unit-weight, and for his unit of volume a cubic centimetre, which is the bulk of a gramme of water. For coarser work, the kilogramme becomes the unit of weight, and the corresponding unit of measure is the litre, which is the bulk of a kilogramme of water. In commercial dealings, in manufacturing processes, and above all in scientific investigations, these simple relations between weights and measures have been found to be an inestimable advantage. The numerical expressions for metrical weights and measures may always be read as decimals. Thus 5.126 metres will be read five metres and one hundred and twenty-six thousandths, and not five metres, one decimetre, two centimetres and six millimetres. The expression 10.5 grammes is read ten and five-tenths grammes ; just as we say one hundred and five dollars, not ten eagles and five dollars ; or sixty-five cents, not six dimes and five cents. All computations under the metrical system are made with decimals alone.

The abbreviations commonly met with in chemical literature are : —

m. m. for millimetre ;	c. m. for centimetre ;
m. for metre ;	c. c. or c. m^3 for cubic centimetre ;
grm. for gramme ;	kilo. for kilogramme.

The equivalents in English weights and measures of those metrical weights and measures which are used in chemistry can be readily found by the aid of the table on the following page, which is available not only for grammes, centimetres and litres, but, by mere change of the position of the decimal point, for all decimal multiples or subdivisions of these quantities.

One cubic metre	=	35.31660	cubic feet.
" " decimetre (a litre)	=	61.02709	" inches.
" " centimetre	=	0.06103	" "
" litre	=	0.22017	imp. gallon.
" "	=	0.88066	" quart.
" "	=	1.76133	" pint.
" "	=	0.26427	U. S. gallon.
" "	=	1.05708	" " quart.
" "	=	2.11415	" " pint.

One pound avoirdupois	=	7000	grains	=	453.59 grm.
" " troy	=	5760	"	=	373.24 "
" ounce avoirdupois	=	437.5	"	=	28.35 "
" " troy	=	480	"	=	31.10 "
" grain				=	64.80 mgrm.
" English imperial gallon	=	277.274	cu. in.	=	4.54 litres.
" U. S. standard gallon	=	231	"	=	3.78 "
" foot				=	0.3048 metre.
" yard				=	0.9144 mgrm.

TABLE FOR THE CONVERSION OF GRAMMES INTO GRAINS, CENTIMETRES INTO INCHES AND LITRES INTO QUARTS.

	1	2	3	4	5	6	7	8	9
Grammes into Grains	15.4323	30.8647	46.2970	61.7294	77.1617	92.5941	108.0265	123.4588	138.8911
Centimetres into Inches	.3937079	.7874158	1.1811237	1.5748316	1.9685395	2.3622474	2.7559553	3.1496632	3.5433711
Litres into Imp. Quarts	0.88066	1.76132	2.64198	3.52264	4.40330	5.28396	6.16462	7.04528	7.92594
Litres into U. S. Quarts	1.05708	2.11415	3.17123	4.22830	5.28838	6.34245	7.39953	8.45660	9.51368

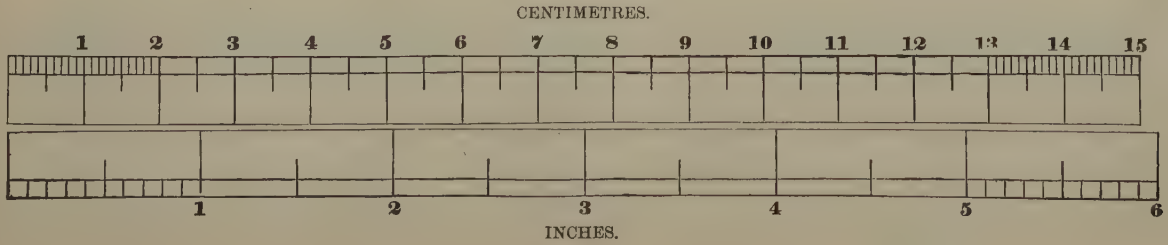


TABLE — *For the Conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.*

Cent	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58.0°	17°	62.6°	60°	140.0°
—45	—49.0	18	64.4	61	141.8
—40	—40.0	19	66.2	62	143.6
—35	—31.0	20	68.0	63	145.4
—30	—22.0	21	69.8	64	147.2
—25	—13.0	22	71.6	65	149.0
—20	— 4.0	23	73.4	66	150.8
—19	— 2.2	24	75.2	67	152.6
—18	— 0.4	25	77.0	68	154.4
—17	+ 1.4	26	78.8	69	156.2
—16	3.2	27	80.6	70	158.0
—15	5.0	28	82.4	71	159.8
—14	6.8	29	84.2	72	161.6
—13	8.6	30	86.0	73	163.4
—12	10.4	31	87.8	74	165.2
—11	12.2	32	89.6	75	167.0
—10	14.0	33	91.4	76	168.8
— 9	15.8	34	93.2	77	170.6
— 8	17.6	35	95.0	78	172.4
— 7	19.4	36	96.8	79	174.2
— 6	21.2	37	98.6	80	176.0
— 5	23.0	38	100.4	81	177.8
— 4	24.8	39	102.2	82	179.6
— 3	26.6	40	104.0	83	181.4
— 2	28.4	41	105.8	84	183.2
— 1	30.2	42	107.6	85	185.0
0	32.0	43	109.4	86	186.8
+ 1	33.8	44	111.2	87	188.6
2	35.6	45	113.0	88	190.4
3	37.4	46	114.8	89	192.2
4	39.2	47	116.6	90	194.0
5	41.0	48	118.4	91	195.8
6	42.8	49	120.2	92	197.6
7	44.6	50	122.0	93	199.4
8	46.4	51	123.8	94	201.2
9	48.2	52	125.6	95	203.0
10	50.0	53	127.4	96	204.8
11	51.8	54	129.2	97	206.6
12	53.6	55	131.0	98	208.4
13	55.4	56	132.8	99	210.2
14	57.2	57	134.6	100	212.0
15	59.0	58	136.4		
16	60.8	59	138.2		

ORDER-LIST OF CHEMICALS.

THE quantities here given are the quantities which one person will use in performing the numbered experiments of this manual according to the directions. In ordering chemicals for a class of several students, a small reduction may be made upon the multiplied quantities. Teachers can get some idea of the cost of these chemicals by referring to the price lists of the "Druggists' Circular," published monthly at 36 Beekman Street, New York, price 13 cents. The names by which the substances are known in commerce are given in the following list; such substances as sugar, starch, marble, &c., do not appear in the list: —

Alcohol	5 oz.
Alum	½ oz.
Ammonia-water (*Aqua Ammonia*)	6 oz.
Ammonium chloride (*sal ammoniac*)	1 oz.
Ammonium nitrate	½ oz.
Aniline	a few drops
Aniline red	a small crystal
Antimony, metallic	30 grains
Arsenious acid	30 grains
Barium chloride	a few grains
Benzol	¾ oz.
Bleaching-powder	2 oz.
Bone-black	3 oz.
Bromine	a few drops
Calcium chloride	1½ oz.
Calcium sulphate (gypsum)	a few grains
Camphor	½ oz.
Castor oil	½ oz.
Carbolic acid (crystallized)	¼ oz.
Carbon bisulphide (*bisulphuret of carbon*)	¼ oz.
Chalk, powdered	½ oz.
Chlorhydric acid	1 lb.
Cochineal	30 grains
Copper (filings)	1½ oz.
Copper oxide	30 grains
Copper sulphate (*blue vitriol*)	30 grains
Ether	1 oz.
Fluor-spar	½ oz.
Gold-leaf	1 sq. inch
Gum-arabic	½ oz.
Indigo	50 grains
Iodine	10 grains
Iron (filings)	1 oz.
Iron sulphate (*copperas*)	¼ oz.
Iron sulphide	1 oz.
Lead acetate (*sugar of lead*)	½ oz
Lead oxide (*litharge*)	2 oz

Litmus . . . . . 15 grains
Logwood, extract of . 30 grains
Magnesium wire . . 4 inches
Manganese, black oxide of 1 oz.
Mercury chloride (*corrosive sublimate*) . . . a few grains
Mercury, red oxide of . . $\frac{3}{4}$ oz.
Nitric acid . . . . . 6 oz.
Nitric acid (fuming) . . $\frac{1}{4}$ oz.
Nutgalls . . . . . $\frac{1}{2}$ oz.
Oxalic acid . . . . 50 grains
Phosphorus, 1 stick, $2\frac{1}{2}$ inches long
Picric acid . . . . 30 grains
Platinum, scrap . . . 10 grains
Potassium, 2 pieces the size of a pea.
Potassium bichromate . . $\frac{1}{2}$ oz.
Potassium bromide . . 1 grain
Potassium chlorate . . . $\frac{1}{2}$ oz.
Potassium cyanide . . 30 grains
Potassium ferrocyanide (*yellow prussiate of potash*) $\frac{1}{4}$ oz.
Potassium hydrate (*white caustic potash*) . . . $\frac{1}{4}$ oz.
Potassium iodide . . . $\frac{1}{16}$ oz.
Potassium nitrate (*saltpetre*) . . . . . 3 oz.
Phosphorus, red . . . 15 grains
Potassium permanganate 6 grains
Potassium tartrate (*cream of tartar*) . . . . . 1 oz.
Rosin . . . . . 30 grains
Shellac . . . . . 40 grains
Sodium, 2 pieces the size of a pea.
Sodium acetate . . . 30 grains
Sodium biborate (*borax*) . $\frac{1}{6}$ oz.
Sodium carbonate . . . $\frac{1}{4}$ oz.
Sodium hydrate (*caustic soda*) . . . . . 1 oz.
Sodium silicate, strong solution (*water-glass*) . 1 oz.
Sodium sulphate (*Glauber's salt*) . . . . . 1 oz.
Strontium nitrate . a few grains
Sulphur, flowers of . . . 1 oz.
Sulphur, roll brimstone . 4 oz.
Sulphuric acid . . . $1\frac{1}{2}$ lbs.
Tin binoxide . . . 15 grains
Turpentine, crude . . . $1\frac{1}{2}$ oz.
Turpentine, oil of . . . 4 oz.
Zinc, granulated or scraps 2 oz.
Zinc filings (or dust) . . $\frac{1}{2}$ oz.
Zinc sheet, two strips 6 by 2 inches.

ORDER-LIST OF UTENSILS.

THE following list includes the utensils which one person will need in performing all the numbered experiments in this manual. The principal articles of steady consumption are glass-tubing, retorts, flasks, corks, caoutchouc-connector and filter-paper. Many of the other articles, once obtained, last a long time. It is evidently not necessary to provide all this apparatus for every member of a large class. Six retorts, as many Woulffe-bottles, four soda-water bottles, two or three measuring glasses, two mortars, two pipettes, one blast-lamp and bellows, three or four pieces of platinum foil, two thermometers, one

pair of scales and one set of weights will suffice, if used with method, for a class of twenty or twenty-five students. Many of the articles can be obtained of the wholesale druggists or of dealers in hardware: for the rest, teachers can consult the priced catalogues of the dealers in philosophical apparatus and chemical ware.

Glass-tubing (App. Fig. 1) —

1 stick about 3 ft. long of No. 1
2 " " " " " 2
½ " " " " " 3
½ " " " " " 4
½ " " " " " 5
2 " " " " " 7
1 " " " " " 8

1 tube about 1 foot long and 1 inch in internal diameter.

[If ignition-tubes can be bought ready made, a dozen of them may be bought instead of one stick of No. 1 and one stick of No. 2 tubing.]

1 retort of 12 oz. capacity with glass stopper.

1 receiver of 8 or 10 oz. capacity with tubulure.

Bottles —

1 wide-mouth bottle, ½ gallon.
1 " " " 1 quart.
1 " " " 1 pint.
2 " " " 8 oz.
2 " " " 4 oz.
2 " " " 2 oz.

1 stout pint bottle with mouth about an inch across, for hydrogen generator.

[These bottles may be of a very common quality, such as are sold as "packing" bottles.]

Funnels —

1 four inches in diameter.
1 two inches in diameter.

3 Woulffe-bottles of about 12 oz. capacity.

Glass flasks —

1 of 1½ pints' capacity
1 of 8 oz. capacity.
2 of 4 oz. capacity.
2 of 2 oz. capacity.

1 thistle-tube.
1 soda-water bottle, stout.
1 conical wine-glass.
6 test-tubes.
1 drying-tube.
1 measuring-glass of 250 c. c. capacity grad. for every 10 c. c.
1 measuring-glass of 25 or 30 c. c. capacity graduated to cubic centimetres.
1 small pipette.
1 nest of 4 or 5 beakers, of which the largest is of 250 c. c. capacity.
2 or 3 bits of window-glass, 3 inches square.

Porcelain evaporating-dishes —

1 about 4 inches diameter.
1 about 2½ inches diameter.
1 deep dish (App. § 21) of 500 c. c. capacity.

1 small iron mortar.
1 Wedgewood mortar about 4 inches in diameter.
1 Bunsen gas-lamp with blowpipe tube (or spirit-lamp where gas is not to be had.)
1 small spirit-lamp.

1 iron ring-stand.
1 piece of iron wire-gauze about 4 inches square.
4 or 5 feet of stout iron wire.
4 feet iron piano-wire.
1 piece fine brass (or copper) gauze about $2\frac{1}{2}$ inches square.
1 iron sand-bath $4\frac{1}{2}$ inches in diameter.
1 water-bath (App. § 17).
1 glass-blower's lamp or Bunsen's gas blast-lamp.
1 small double acting bellows.
1 mouth-blowpipe.
1 triangular file.
1 round file.
1 pair jewellers' tweezers.
1 piece platinum foil $1\frac{1}{2}$ inches square.
1 piece platinum wire 4 inches long, and not thicker than a No. 5 needle.
1 stoneware milk-pan.
1 flower-pot saucer (or two bits of wood 6 inches by 3 inches by 1 inch, loaded with lead).
1 Hessian crucible of about 8 oz. capacity.
1 lead pan for Exp. 41.
1 common plate.
1 soup plate.
1 thermometer.
1 pair of small scales ("Tea"-scales for grocers' use).
1 set of gramme weights 1, 2, 5, 10, 20 and 50 grammes.
Corks — an assortment of various sizes, to fit the ignition-tubes, the flasks, the hydrogen generator, &c.
Caoutchouc tubing —
1 foot of $\frac{1}{8}$ inch.
1 foot of $\frac{3}{16}$ inch.
4 feet of $\frac{1}{4}$ inch.
1 iron spoon.
1 pair wooden nippers.
4 sheets of common filter-paper, or 2 sheets of filter-paper and half a bunch of cut filters 3 inches in diameter.

INDEX.

The following abbreviations are used in this index ; *occ.* stands for occurrence ; *prep.* for preparation ; *prop.* for properties ; *comp.* for composition ; *def.* for definition. The numbers refer to the pages ; the Roman numerals to the Appendix.

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